

Pore water chemistry of a Paleogene continental mudrock in Spain and a Jurassic marine mudrock in Switzerland: Sampling methods and geochemical interpretation

Química del agua intersticial de una arcilla continental Paleógena en España y una arcilla marina Jurásica en Suiza: métodos de muestreo e interpretación geoquímica

M.J. Turrero^{1*}, A.M. Fernández¹, J. Peña¹, M.D. Sánchez², P. Wersin³, P. Bossart⁴, M. Sánchez², A. Melón¹, A. Garralón¹, A. Yllera¹, P. Gómez¹, P. Hernán⁵

¹ Dpto. de Medioambiente, CIEMAT, Avda. Complutense 22, 28040 Madrid, Spain

² Dpto. de Tecnología, CIEMAT, Avda. Complutense 22, 28040 Madrid, Spain

³ NAGRA, Hardstrasse 73, CH-5430 Wettingen, Switzerland

⁴ Geotechnical Institute Ltd, CH - 2882 St-Ursanne, Switzerland

⁵ ENRESA, Emilio Vargas, 7, 28043 Madrid, Spain

*corresponding author: mj.turrero@ciemat.es

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Abstract

This work summarises the methodologies and approaches developed in CIEMAT during the last 10 years for the characterisation of argillaceous formations with the aim of obtaining information on their pore water composition. The work is focused on two sedimentary formations: the Opalinus Clay from Switzerland and an Oligocene-Miocene Clay from Spain, with rather different characteristics as much from the point of view of the methodology applied to the study as for the sedimentary origin itself of both formations.

The Swiss clay was studied through the participation in the DI-B experiment carried out at the Mont Terri Underground Rock Laboratory, in Switzerland. This experiment was devoted to water sampling and in situ analysis of pore water. Samples were collected and analysed after developing equipments and methodologies to minimize the perturbation of the critical parameters of the clay pore water: pH, Eh, pCO₂, Fe(II) and alkalinity. Geochemical modelling is used to interpret and understand the main geochemical processes controlling the water chemistry and the present state of the system.

Concerning the Spanish clay, the work shows the development of an integrated methodology to characterize a clay formation from core samples belonging to one borehole, named S1. The study integrates all the available data on pore water composition, based on squeezing and leaching experiments, with the mineralogy and geochemistry studied from the mentioned core samples. Geochemical modelling was employed with two main objectives: to check the consistency of the pore water analytical data and to determine the relative importance of the main processes governing the chemistry of the pore water. Specifically, it was used to simulate the processes controlling the redox evolution in the clay formation. The simulation considered equilibrium for reactive minerals such as calcite, dolomite, gypsum and ferrihydrite. Microbially-mediated degradation of organic matter and oxidative dissolution of pyrite were also considered from a kinetic point of view.

Keywords: clays, pore water, borehole equipment, squeezing, geochemistry, modelling

Resumen

Este trabajo resume una serie de metodologías y aproximaciones desarrolladas en CIEMAT durante los últimos 10 años con el objetivo de obtener información del agua intersticial de dos formaciones arcillosas: la Opalinus Clay procedente de Suiza y una

formación de edad Oligoceno-Mioceno española. Ambas tienen características bastante diferentes tanto desde el punto de vista de la metodología aplicada para su estudio como del origen sedimentario en sí mismo de las dos formaciones.

La arcilla Suiza se estudió a través de la participación en el experimento DI-B en el laboratorio subterráneo de Mont Terri, en Suiza, uno de cuyos objetivos fue el muestreo y análisis *in situ* del agua intersticial de la arcilla. Las muestras de agua se recogieron después de desarrollar equipos y metodologías para conseguir una alteración mínima de los parámetros críticos del agua de la arcilla: pH, Eh, $p\text{CO}_2$, Fe(II) y alcalinidad. La modelización geoquímica se utilizó como herramienta para interpretar y entender los principales procesos geoquímicos que controlan la química del agua y el estado actual del sistema.

En relación con la arcilla española, el artículo muestra el desarrollo de una metodología integrada para caracterizar el agua intersticial de la formación arcillosa a partir de muestras de testigos correspondientes a un sondeo, denominados S1. El estudio trata de integrar todos los datos disponibles sobre la composición del agua intersticial obtenida mediante la técnica de compresión bajo presión (*squeezing*) y mediante extractos acuosos, con la caracterización mineralógica y geoquímica de los testigos. La modelización geoquímica se utilizó con dos objetivos principales: para valorar la consistencia de los datos analíticos del agua intersticial y para determinar la importancia relativa de los principales procesos que gobiernan la química del agua intersticial. Específicamente, la modelización se utilizó para simular los procesos que controlan la evolución redox del sistema. Se consideró equilibrio para los minerales reactivos como la calcita, dolomita, yeso y ferrihidrita. Además, se trató la degradación de la materia orgánica y la disolución oxidativa de la pirita desde un punto de vista cinético.

Palabras clave: arcillas, agua intersticial, instrumentación de sondeos, compresión bajo presión, geoquímica, modelización

1. Introduction

At present, the deep geological disposal (DGD) is the most promising choice of management of radioactive wastes. It is a technically feasible option and provides the long-term isolation and protection of the radioactive waste (Chapman, 2006). The DGD involves a system of natural and engineered barriers to isolate the wastes from the environment. The disposal strategies include, as one of the possible natural barrier alternatives, argillaceous formations as host rocks. Different countries are investigating various aspects on selected formations in order to evaluate if this alternative is reliable regarding safety purposes.

If a failure of any engineered barrier occurs, the natural barrier plays an important role in retaining radionuclides. In addition, considering the mass balance of the geological system, the natural barrier can dilute strongly the pollution. In argillaceous formations, it has been demonstrated that radionuclide transport will be dominated by diffusion and the migration will be retarded by the high sorption capacity of the clays (e.g. Bonne and Heremans, 1981; Chapman and McKinley, 1987; Horseman, 1994; Savage, 1995; Mazurek *et al.*, 2003). Furthermore, multiple coupled processes of water-clay interactions as well as osmotic behaviour in these clay-rich formations control solubility, speciation and mobility of radionuclides. For this reason, an exhaustive knowledge on the bulk and clay mineralogy of mudrocks, their ion exchange capacity and hydrogeochemical characteristics (pH, redox state, chemistry of the solution, presence of colloids and complexes, etc.) is essential for assessing argillaceous formations as part of a geological disposal system of hazard wastes.

Among the countries that are undertaking or have accomplished research programs on consolidated or plastic argillaceous formations are: France (Toarcian-Domerian Clay at Tournemire and Callovo-Oxfordian Clay at Bure), Belgium (Boom Clay at Mol), Hungary (Boda Clay at Mecsek), Switzerland (Opalinus Clay at Mt Terri and Palfris Formation at Wellenberg), Japan (Wakanai and Koetoi formations at Honorobe), United Kingdom (Oxford Clay) and United States of America (Pierre Shale in South Dakota). Based on these studies, considerable progress in the development of techniques for hydrology, geochemistry and hydrogeochemistry of mudrocks has been accomplished (e.g. Entwisle and Reeder, 1993; Gautschi and Scholtis, 1989; Beaufais *et al.*, 1994; De Windt *et al.*, 1998; Bradbury and Baeyens, 1998; Thury and Bossart, 1999; Sacchi and Michelot, 2000 (review), 2001; Bath, 2001; Gaucher *et al.*, 2002, 2004, 2006; Pearson *et al.*, 2003; Wersin *et al.*, 2004; Vinsot *et al.*, 2005) with important advances in the knowledge of geochemical processes in these systems and their evolution over time (e.g. Reeder *et al.*, 1993; Baeyens and Bradbury, 1994; Beaucaire *et al.*, 2000; Pearson *et al.*, 2003).

The methods for collecting water from mudrocks, either *in situ* or in the laboratory, may affect the chemistry of the water (Baeyens *et al.*, 1985; McCarthy and Degueudre, 1993; Appelo and Postma, 1996; Pearson *et al.*, 2003; de Craen *et al.*, 2004). The main problems usually found in low permeability geological systems for groundwater sampling and chemical characterisation are related to outgassing and oxidation of the samples (e.g. Almen *et al.*, 1986; Griffault *et al.*, 1996; Degueudre *et al.*, 1999; Laaksoharju, 1999; Arcos *et al.*, 2001; Fernández *et al.*, 2001a; Peña *et al.*, 2001; Pearson *et al.*, 2003; Wersin *et al.*, 2004), which lead to variations in key parameters

such as pH, alkalinity, redox potential or sulphate concentration. On the other hand, the lack of measurements of organic matter either of anthropogenic origin (e.g. drilling machinery, downhole equipment to sample, etc.) or naturally present in the formations can mislead the interpretation of alkalinity measurements (e.g. Merino, 1979; Eichinger and Wersin, 2004). Cation exchange reactions exert an important control on the chemistry of water in clay-rich rocks as well. To model water chemistry in such rocks requires knowledge of the concentration of exchangeable cations in the formation. However, measurement of concentrations of individual exchangeable cations is experimentally difficult for a number of reasons; for example, the presence in the clayey systems of minerals such as carbonates and/or sulphates. When placed in water, these minerals could react to some extent. The thereby dissolved cations react with the exchangeable cations originally present in the rock and change their relative concentrations (Thomas, 1982; Fernández *et al.*, 2001b; Waber *et al.*, 2003).

All these facts make it difficult to correctly interpret measurements made in the field or in the laboratory for safety assessment purposes. The uncertainties can be checked and rationalized assuming geochemical constraints, which are supported by a complete characterisation of the system based on collection of samples at different points and long-term monitoring (e.g. Horseman *et al.*, 1992; Griffault *et al.*, 1996; Arthur and Wang, 2000; Pearson *et al.*, 2003). At this point, geochemical modeling is the most common tool to interpret and understand the processes controlling the evolution of water chemistry (e.g. Beaucaire *et al.*, 1995; Pearson *et al.*, 1998; Waber *et al.*, 1998; Tempel and Harrison, 2000; Arcos *et al.*, 2001; Pearson *et al.*, 2003; Gaucher *et al.*, 2006). The use of geochemical modeling tools helps to determine the physicochemical and compositional reconstruction of the formation pore waters as well as their evolution.

The hydrogeochemical characterization of an Oligocene-Miocene Clay from N Spain has been an objective of the Spanish research program. Furthermore, Spain takes part in the Swiss research program studying the Opalinus Clay, and is involved in the characterization of the Callovo-Oxfordian Clay and the Boom Clay through the Integrated Project *Fundamental Processes of Radionuclide Migration* (Sixth Framework Programme of the European Commission).

This work presents a summary of the methodologies and approaches applied to study the pore water of two sedimentary formations (Opalinus Clay from Switzerland and an Oligocene-Miocene Clay from Spain) with rather different characteristics as much from the point of view of the methodology applied to the study as for the geolog-

ical history of both formations. The methodological advances and results of the two argillaceous formations are presented. The work is part of a research program funded by ENRESA/NAGRA, on one hand, and, ENRESA on the other, in the context of their R&D programs.

The Swiss clay is studied through the participation in the Mont Terri international research project¹, which is part of the strategy of development of methodologies to characterize *in situ* argillaceous formations, and study the geochemical aspects of these formations. The project is structured as a series of individual experiments in the fields of geology, hydrogeology, geochemistry and rock mechanics. The experimental objectives cover, on one hand, the general testing of tools and methods for the investigations in clay-rich formations and, on the other hand, the characterisation specifically of the Opalinus Clay formation. After the lessons learned in the Mont Terri Rock Laboratory concerning the methods to investigate the water chemistry and the chemical evolution of claystones (Pearson *et al.*, 2003), attention is focused in this paper to the results obtained from the experiments devoted to water sampling and analysis by different *in situ* and laboratory methods, with the goal of minimizing the alteration of the samples due to outgassing and oxidation during sampling. We focus specifically on water samples collected from the DI-B experiment, in its part dedicated to *in situ* hydrogeochemical characterisation.

Concerning the Spanish clay, the work shows the development of an integrated methodology to characterize a clay formation from core samples belonging to one borehole named S1. The study integrates all the available data on pore water composition, based on squeezing and leaching experiments, with the mineralogy and geochemistry studied from the mentioned core samples. A conceptual model on the evolution of the water-rock reactions is proposed. Then geochemical modelling is employed with two main objectives: to check the consistency of the pore water analytical data and to determine the relative importance of the main processes governing the chemistry of the pore water.

2. Geological aspects of the studied sites

2.1. Opalinus Clay (Switzerland)

The studies on the Opalinus Clay were carried out in an underground laboratory (the reconnaissance gallery of a motorway) constructed in the Jura Mountains, in north-

¹ Run as a consortium of partners: NAGRA (Switzerland), ANDRA and IRSN (France), JNC and Obayashi (Japan), SCK-CEN (Belgium), BGR and GRS (Germany), ENRESA (Spain). The investigations within the project are carried out under the patronage of the Swiss Geological Survey.

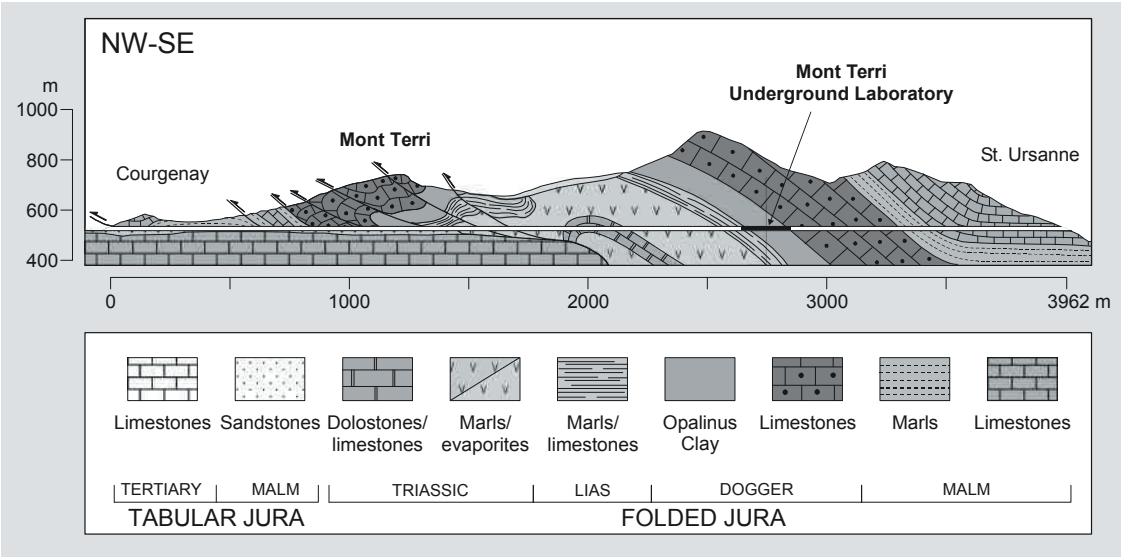


Fig. 1.- Geological profile through the Mont Terri anticline, with the stratigraphic sequence in which the Opalinus Clay formation is located (Bath and Gautchi, 2003).

Fig. 1.- Perfil geológico del anticlinal de Mont Terri, con la secuencia estratigráfica en la que se encuentra la formación Opalinus Clay (Bath and Gautchi, 2003).

western Switzerland. The stratigraphic section includes rocks with Triassic-Jurassic age (Fig. 1). The Opalinus Clay is an indurated clay, upper Aalenian (180-170 Ma), deposited in a shallow marine environment. It is underlain by marls-limestones (Toarcian) and overlain limestones (upper Aalenian/lower Bajocian). The geological history is described in Tripet *et al.* (1990), Bossart and Wermeille (1999) and Bath and Gautchi (2003). The porosity ranges from 5 to 20 % (Mazurek, 1999), including

total (water content) and geochemical/transport porosity. The hydraulic conductivity values of the intact Opalinus Clay are in the range of 2×10^{-14} - 2×10^{-12} m/s (Marschall *et al.*, 2004).

The mineralogical composition consists of an average of 45-76 % of phyllosilicates (illite, illite/smectite mixed layers, chlorite and kaolinite), along with 6-39 % of calcite and 6-30 % of quartz. Other minerals present are siderite (~1-4%), plagioclase and K-feldspar (~2-4%),

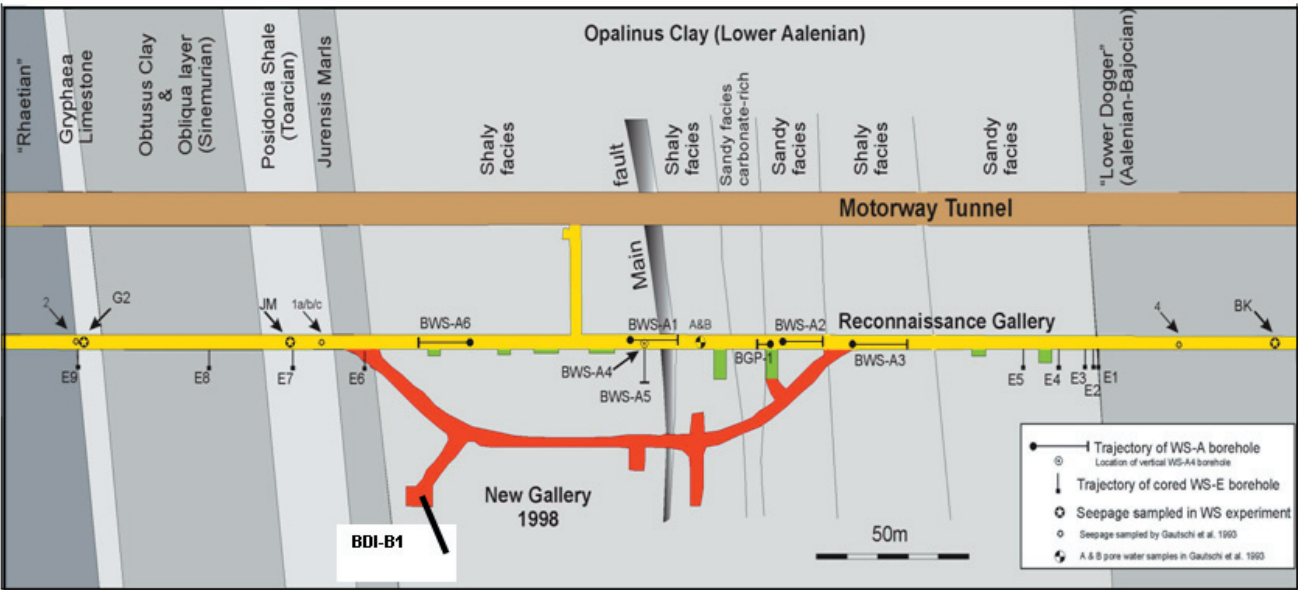


Fig. 2.- Schematic plan along the Mont Terri Rock Laboratory. BDI-B1 borehole is located at the DI niche. The location of other water sampling (WS) boreholes is also shown (Bath and Gautchi, 2003).

Fig. 2.- Planta del Laboratorio Subterráneo de Mont Terri. El sondeo BDI-B1 está localizado en el nicho DI. En la figura se muestra la localización de otros sondeos en los que se han tomado muestras de agua (WS) (Bath and Gautchi, 2003).

Mudrock	Oligocene-Miocene Clay ¹	Opalinus Clay ²
Location	North-Central Spain	Mt Terri
Classification	Plastic red to green massive clays with sandy admixtures	Indurated dark-gray silt/sandy claystone
Depth	82 – 145 m	230 – 320 m
Country	Spain	Switzerland
Age	Oligocene-Miocene	Jurassic (180 – 178 m.a.)
Origin	Continental	Marine
Thickness	300 – 350 m	160 m
Overlain Fm	Low-permeable marls with gypsum	Dogger Limestones
Underlain Fm	More permeable marls	Liassic marls and limestones
Clay minerals	30 – 80 % (smectite, illite, chlorite, kaolinite)	55 – 80% (illite, illite/smectite, kaolinite, chlorite)
Carbonates	7 – 48 % (calcite, dolomite)	6 – 31% (calcite, dolomite/ankerite, siderite)
Other minerals	Q (1 – 30 %), gypsum, pyrite, organic matter	Q (15 – 30%), feldspar, pyrite, organic matter
CEC	16 – 49 meq/100g	9 – 13 meq/100g
Dry density	1.7 – 2.1 g/cm ³	2.2 – 2.4 g/cm ³
Total porosity	24 – 39 %	12 – 19 %
Permeability	$\approx 2 \times 10^{-11} - 1 \times 10^{-12}$ m/s	$\approx 2 \times 10^{-12} - 2 \times 10^{-14}$ m/s
Dominant transport mechanism	Diffusion	Diffusion
Specific Surface Area (N ₂ -BET)	29 – 58 m ² /g (external)	24 – 37 m ² /g (external)
Water type	Na-SO ₄ ²⁻	Na-Cl ⁻
Ionic strength	0.2 – 0.3 mol/L	0.1 – 0.4 mol/L
[Cl ⁻] mg/L	1000	4000-10000
Organic matter	0.7 – 4.1 % (CO ₂ org.)	5 – 15 mg/L DOC

¹López-Geta et al., 1994, Pelayo *et al.*, 2003, Peña *et al.*, 2003, Proyecto AFA, 1995; ²Bossart and Thury, 1998, Mazurek, 1998, 1999, Cottour *et al.*, 1999, de Windt and Palut, 1999, Thury and Bossart, 1999a, Bock, 2001, Pearson *et al.*, 2003.

Table 1.- Main characteristics of the clays selected for this study.

Tabla 1.- Principales características de las arcillas seleccionadas para este estudio.

and other minerals in trace amounts such as aragonite, biotite, moscovite, apatite, celestite, zircon and monazite. The contents of pyrite and organic matter vary between 0.7-3.2 wt.% and 0.1-1.5 wt.%, respectively (Gaucher *et al.*, 2003). The cation exchange capacity ranges from 9 to 13 meq/100g (Waber *et al.*, 2003). Table 1 shows a synthesis of the main characteristics of the formation.

The *in situ* experiment for water sampling is located at the end of the DI niche within the New Gallery of the Mont Terri Rock Laboratory (Fig. 2). The rock in this zone is part of the lowest Opalinus Clay units, the so-called shaly facies; and is situated a few meters away from the underlying formation (Jurensis Marl, Toarcian). The salinity in this zone is the highest in the shale formation with 12 g/L of chloride (Fig. 3), and the physical

porosity and water content of the rock are around 17% and 7 wt.%, respectively (Pearson *et al.*, 2003).

2.2. Oligocene-Miocene Clay (Spain)

The clays investigated are alluvial to lacustrine sediments of Oligocene-Miocene age and occur throughout North-Central Spain, in a continental and mainly endorheic environment. It is a plastic clay formation, with a thickness of around 300 m, occurring at depths below 80 m. The total porosity ranges from 15 to 40 % (Villar, 2003) and the hydraulic conductivity is estimated from one borehole testing to be $2 \times 10^{-11} - 1 \times 10^{-12}$ m/s (López-Geta *et al.*, 1994).

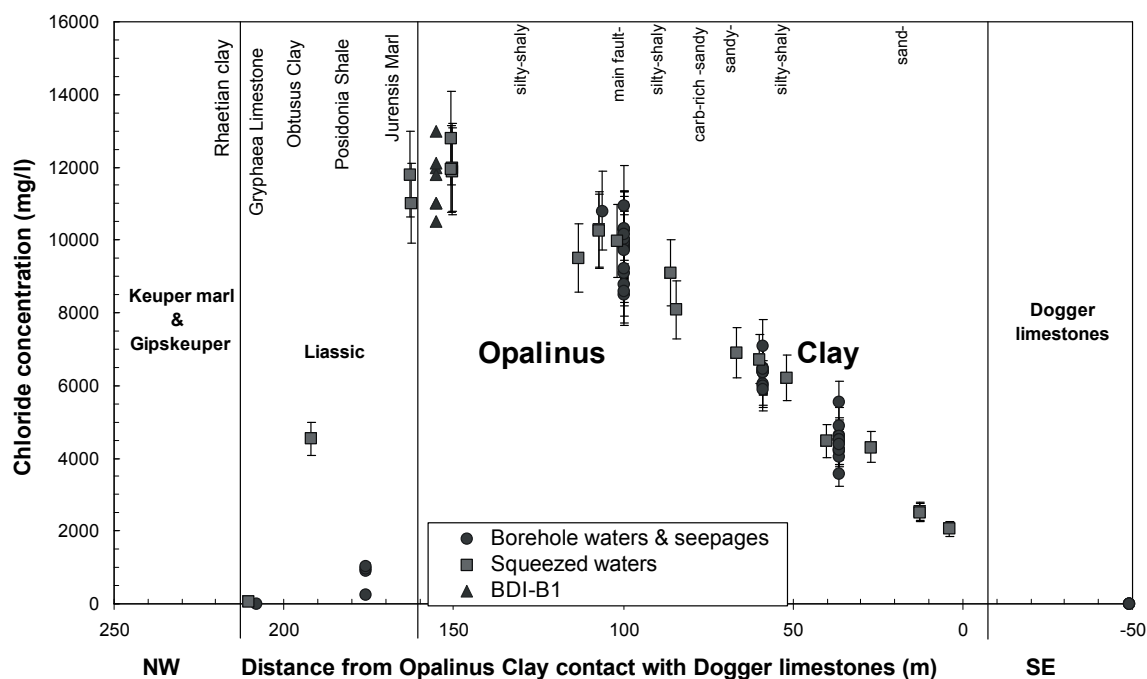


Fig. 3.- NW-SE cross-section profiles of chloride concentrations in Opalinus Clay pore waters. Up triangles represent the values measured in the seep water from borehole BDI-B1 in different sampling campaigns (modified from Pearson *et al.*, 2003).

Fig. 3.- Perfil NW-SE de la concentración de cloruro en el agua intersticial de la Opalinus Clay. Los triángulos representan los valores medidos en el agua recogida en el sondeo BDI-B1 en diferentes campañas de toma de muestras (modificado a partir de Pearson *et al.*, 2003).

The material for the study consists of one well, named S1 (650 m depth) (Fig. 4), which comprises a 106 m thick basal lutite sequence dominated by red and green lutites, with some sandstone alternations deposited by fluvio-alluvial processes. The upper part is a 198 m thick lutite to marl sequence, with gypsum and carbonates increasing towards the top, deposited in a predominantly lacustrine environment. It is underlain by terrigenous facies and overlain by marls/limestones with gypsum (lower part).

The composition of the clays is briefly described in Pelayo *et al.* (2003). Mineralogical composition of the basal sequence of the clay formation consist of 10-30 % quartz, 6-30 % calcite, 1-4 % dolomite, 50-70 % clay minerals (0-2 % smectite, 85-90 % illite and 10-12 % chlorite/kaolinite) and accessory feldspars, gypsum, barite, celestite, ilmenite, iron oxy-hydroxides and pyrite; the upper part of the clay consists of 2-9 % quartz, 6-38% calcite, 0-8 % dolomite, 45-65 % clay minerals (45-60 % illite, 30-50% smectite and 3-7 % chlorite/kaolinite), 2-4 % gypsum and accessory feldspars, barite, celestite, iron oxy-hydroxides, ilmenite and pyrite.

Gypsum has been identified to occur dispersed in the matrix in all the samples analyzed and anhydrite occurs in the deepest samples (e.g. Fig. 5). Most of the iron analyzed in the solid samples is in the <2 μm fraction, as part of the illite structure (e.g. $(\text{Si}_{3.375}\text{Al}_{0.625})(\text{Al}_{1.595}\text{Fe(III)}_{0.255}\text{Mg}_{0.26})\text{O}_{10}(\text{OH})_2(\text{Ca}_{0.03}\text{K}_{0.49})$), or in the smectite (e.g. $(\text{Si}_{3.395}\text{Al}_{0.605})(\text{Al}_{0.69}\text{Fe(III)}_{0.32}\text{Mg}_{1.555})\text{O}_{10}(\text{OH})_2(\text{Ca}_{0.11}\text{K}_{0.24})$) and in chlorite. Only a small part of the iron is present as iron oxides (e.g. goethite was detected in the deepest samples) or pyrite, usually altered, mainly in the upper part of the stratigraphic column.

Isotopic results on gypsum and carbonates from borehole S1 and another borehole in the area (borehole S2, not included in this work) (Fig. 6) fits to the meteoric water line, and indicates the gap between the results of the upper and the lower part in the borehole. This fact suggests that no connection between both parts exists. Thus, we assume that the isotopic data reflect equilibrium conditions from the moment in which deposits were buried. This situation should be maintained nowadays.

Table 1 shows a synthesis of the main features of the formation.

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3. Field and laboratory sampling and analysis of pore water

The pore water was extracted directly from boreholes with specific downhole equipment (case of Opalinus Clay; Fernández *et al.*, 2006) or from clay cores by means of *squeezing* (case of Oligocene-Miocene Clay). Additional analyses of aqueous extracts, cation exchange capacity and geochemical modelling allowed draw up the geochemical behaviour of the systems.

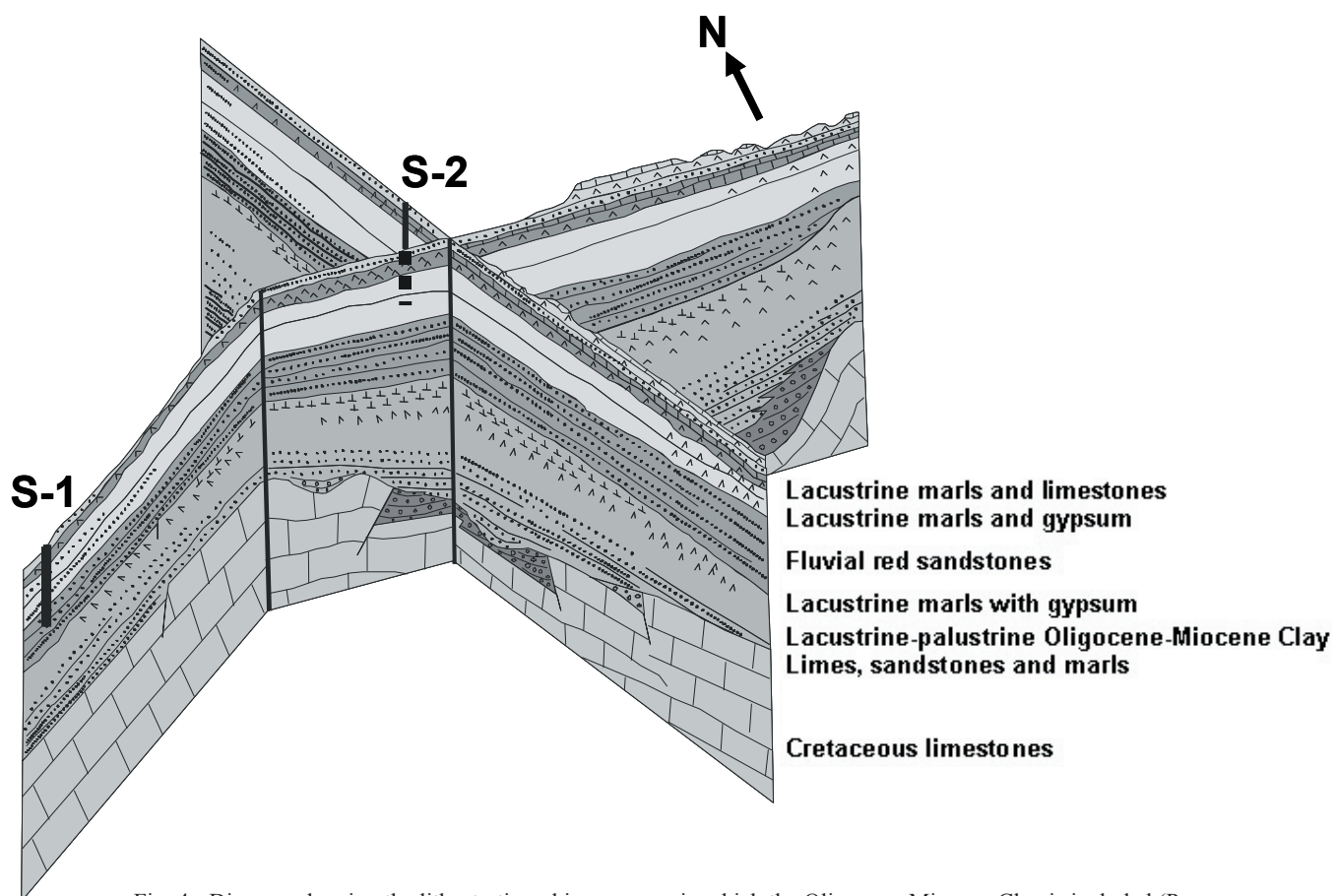


Fig. 4.- Diagram showing the lithostratigraphic sequence in which the Oligocene-Miocene Clay is included (Proyecto AFA, 1995).

Fig. 4.- Diagrama en el que se muestra la secuencia litoestratigráfica en la que se incluye la arcilla del Oligoceno-Mioceno (Proyecto AFA, 1995).

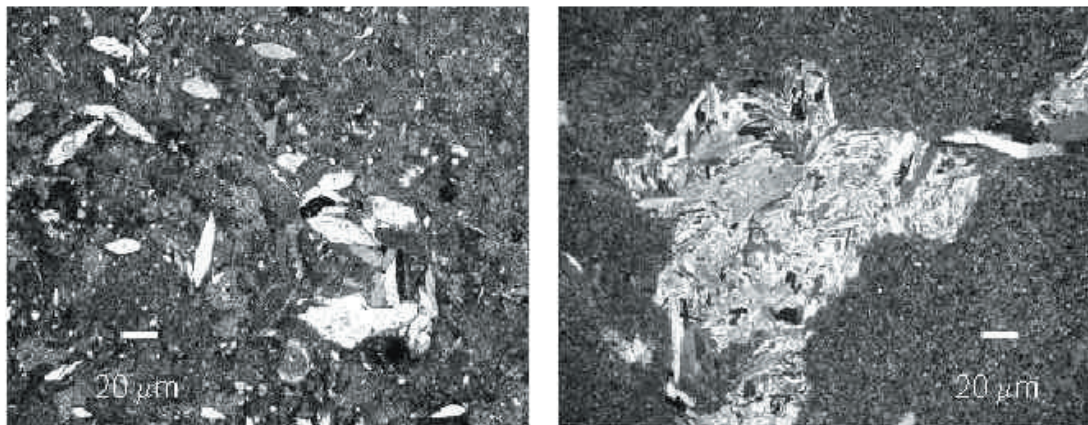


Fig. 5.- Optical microscope photographs of Oligocene-Miocene Clay. (Left) Prismatic crystals of gypsum micro-lenticular, dispersed or forming aggregates. There is a high content of iron oxy-hydroxides. (Right) Aggregate of brilliant colours, corresponding to anhydrite, distinguished on gypsum crystals (Peña *et al.*, 2003).

Fig. 5.- Fotografías de microscopio óptico de la arcilla del Oligoceno-Mioceno. En la imagen de la izquierda se observan cristales de yeso prismático, de tendencia microlenticular, dispersos y en agregados. Se observa, además, un alto contenido en oxihidróxidos de hierro. En la imagen de la derecha se observa un agregado de colores vivos, correspondiente a anhidrita, que destaca sobre los cristales grises de yeso (Peña *et al.*, 2003).

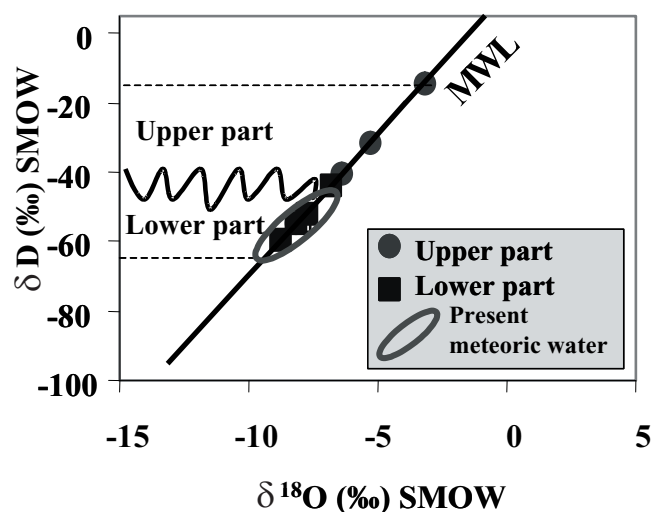


Fig. 6.- Isotopic composition ($^{18}\text{O}/^2\text{H}$) (‰ SMOW) calculated from carbonate and gypsum extracted from the cores of boreholes S-1. The Meteoric Water Line (MWL) is represented for the studied area (Pelayo *et al.*, 2003).

Fig. 6.- Composición isotópica ($^{18}\text{O}/^2\text{H}$) (‰ SMOW) calculada a partir de los carbonatos y los yesos extraídos de los testigos del sondeo S-1. Se representa la línea de aguas meteóricas (MWL) y el agua meteórica actual en el área de estudio (Pelayo *et al.*, 2003).

3.1. Field methods for extracting and analyzing water (Mont Terri Rock Laboratory)

One of the main objectives of the participation in the program on geochemical studies at the Mont Terri Rock Laboratory through the Mont Terri project was to collect water representative of the on site conditions by sampling a borehole interval. After considering the recommendations by Pearson and Bath (2003) for obtaining reliable samples from boreholes, samples were collected and analysed after developing equipments and methodologies to avoid oxygen or air contact with the formation samples. The goal was sampling with a minimum perturbation of the clay pore water critical parameters: pH, Eh, pCO_2 , Fe(II) and alkalinity.

For this purpose, the borehole BDI-B1 (20 m length) was drilled two meters from the floor towards the roof of the DI niche within the New Gallery of the Mont Terri Rock Laboratory. It was drilled with pressurized air as drilling fluid and with a single core barrel. A certain time was required to isolate the borehole to obtain reliable pore water samples. During that time, besides drilling works, the borehole was open to air sporadically, until its definitive closing. At this point, the borehole was equipped with a downhole single packer in order to maintain it isolated from air until designing the definitive downhole system for long-term monitoring and sampling. The tritium measurements made in the water sampled in this pe-

riod fell from 3.8 T.U. to <0.7 T.U. (Fig. 7). Tritium was analysed in other boreholes (Pearson *et al.*, 2003) and results were <0.8 T.U., indicating a residence time for the sampled water to be higher than 60 years.

The downhole equipment was specially designed to obtain samples of water seeping at very low rates from the rock. As a complement, surface equipment controled the functions of the downhole equipment and made it possible to take unaltered samples.

The downhole equipment was made up of the following components (Fig. 8): (1) An inflatable packer placed roughly at 7.75 m from the borehole mouth, which isolates the water sampling interval, located between the packer and the end of the borehole. This sampling interval was equipped with seven external rigid PVC tubes with 200 μm slots. Due to the low water volume expected, a tube of POM (Polyoxymethylene Tecaform Delrin) was placed inside the PVC tube to collect the scarce seepage water, thus avoiding the dead volumes inside the PVC tube. At the end of this central tube, four valves were connected to different PFA (Perfluoroalkoxy) tubing (an inert material impervious to O_2 diffusion) for water sampling, water pressure monitoring in the section, gas inflow (the test interval was flushed with argon) and gas outflow; and (2) An inflatable packer positioned closing the borehole mouth. The space between the two packers was filled with six rigid tubes of PVC to avoid the collapse of the borehole and to increase the hydraulic gradient in the sampling interval. The end-packer was connected up to the mouth of the borehole with a 1 m long PVC rigid tube. The four PFA tubing were guided from the test interval through this PVC tube, which was sealed with epoxy resin at the end, in the tunnel wall.

All the tubing for the water and gas lines were guided towards the equipment installed at surface, which is composed of the following elements (Fig. 9): (1) A packer system control unit equipped with: a three-way valve and a manual manometer for packer inflation pressure control, and a DRUCK transducer connected to a data acquisition system for controlling that the packer keeps the pressure. (2) A vacuum pump system for generating an under-pressure in the sampling interval in order to increase the hydraulic gradient towards the sampling zone. A vacuum transducer is installed in the gas outflow tube to measure the vacuum pressure in the sampling interval for controlling interval tightness. (3) A gas pressure regulator system with two functions: to flush the gas ($\text{Ar}+1\% \text{CO}_2$ mix used in the first campaigns or Ar used afterwards) in the sampling interval through the gas tubing and to keep the anoxic conditions in the glove box. A semi-automatic gas control unit with a gas inlet with maximum pressure of

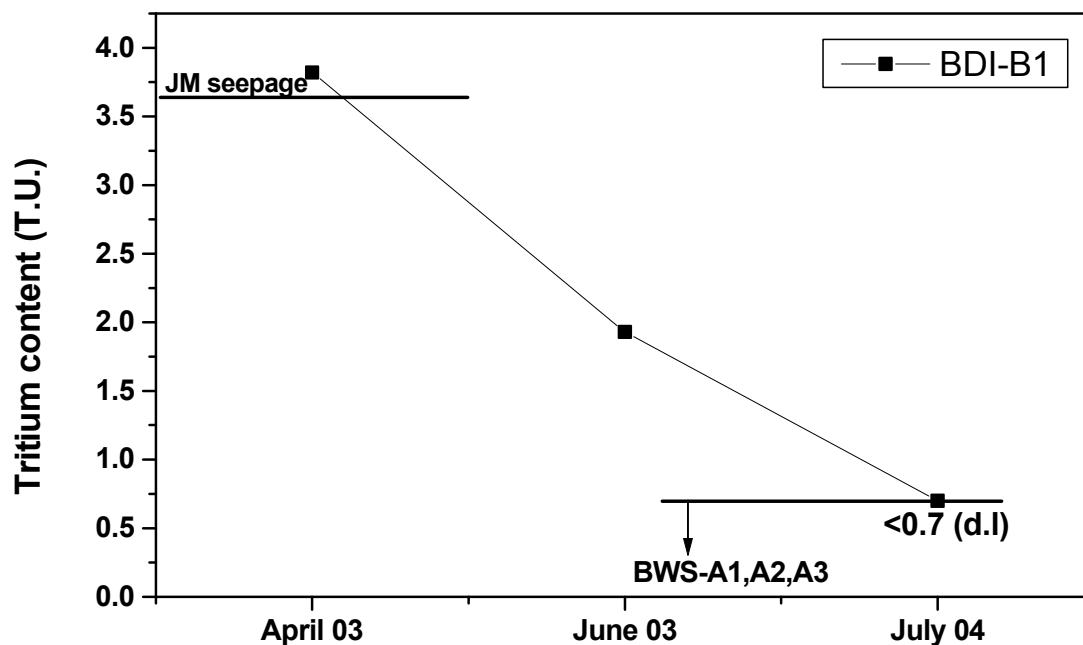
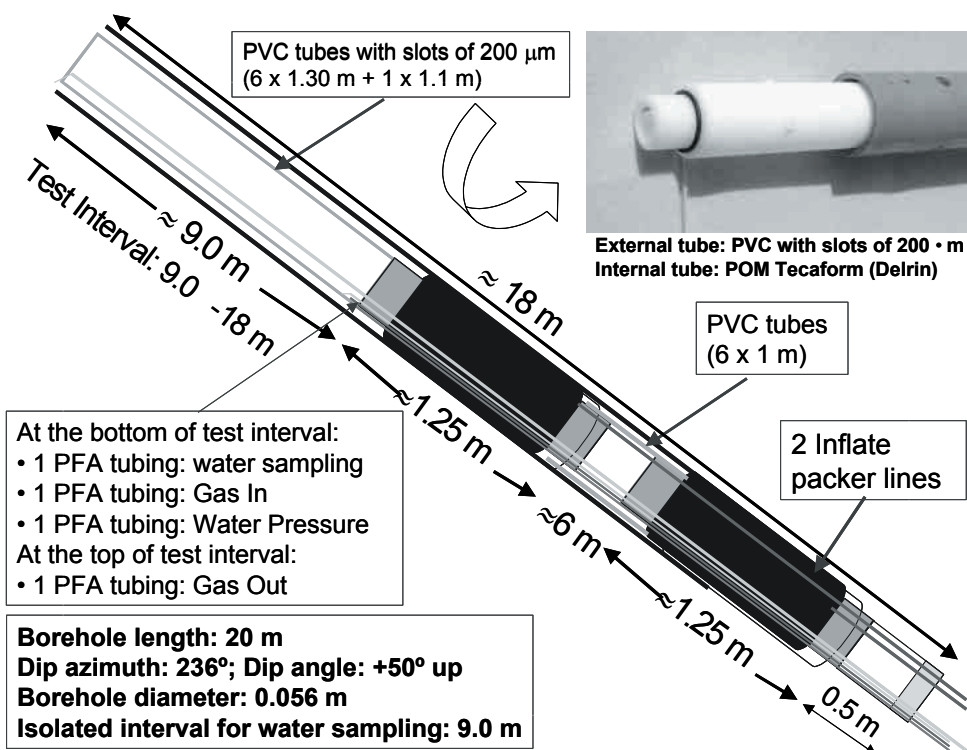


Fig. 7.- Evolution of the tritium content in the water of borehole BDI-B1 in the first water samples. Horizontal lines represent tritium values obtained from underlying Jurensis Marl seepage and from boreholes BWS-A1, A2 and A3 (data extracted from Pearson *et al.*, 2003).

Fig. 7.- Evolución del contenido en tritio en el agua del sondeo BDI-B1 en las primeras campañas de recogida de muestras. Las líneas horizontales representan los valores de tritio obtenidos de la formación infrayacente Jurensis Marl y de los sondeos BWS-A1, A2 y A3 (datos extraídos de Pearson *et al.*, 2003).

Fig. 8.- Downhole equipment installed in borehole BDI-B1.

Fig. 8.- Equipo instalado en el interior del sondeo BDI-B1.



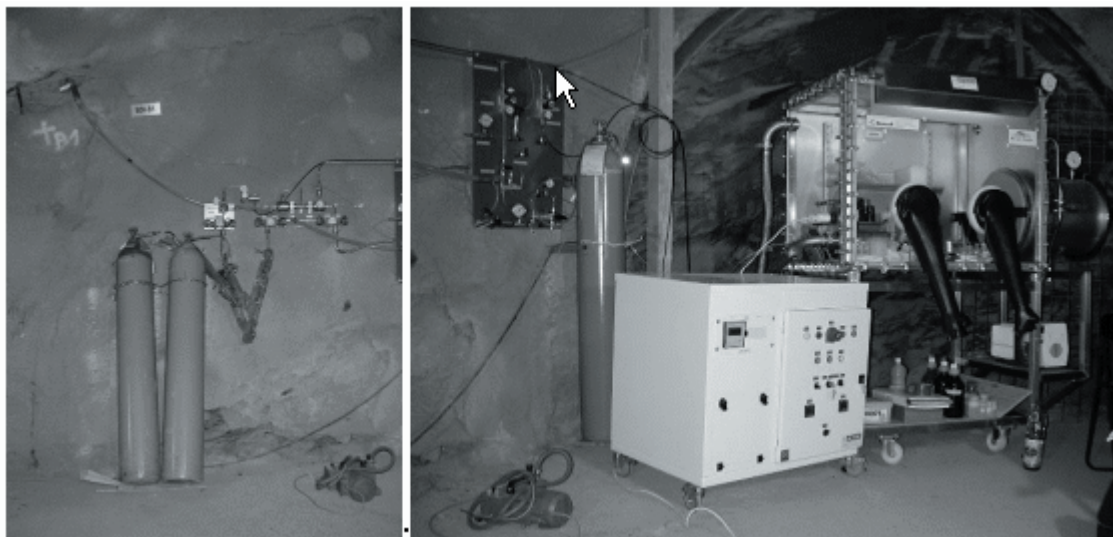


Fig. 9.- Surface instrumentation installed in borehole BDI-B1 for controlling the operation of the downhole equipment and for analysing and sampling in anoxic conditions.

Fig. 9.- Equipo instalado en superficie próximo al sondeo BDI-B1 para el control del equipo instalado en el interior y para el muestreo y análisis en condiciones anóxicas.

250 bar and a pre-regulated gas outlet of 8 bar is used for gas flushing and feeding the anoxic glove box. Another gas regulator system is used for the regeneration process of the anoxic glove box with an Ar+1% H₂ gas mixture. (4) A water pressure measurement control unit measures the water pressure in the sampling interval. It is equipped with a three-way valve, a manual manometer and a DRUCK PMP 4070 pressure transducer (amplified output, 0-10 bar abs., $\pm 0.04\%$ accuracy). (5) A data acquisition system, which is connected to a dial-up router, records the water and the packer pressures. This configuration makes possible access to the operation of the equipment via modem. (6) An anoxic glove box (JACOMEX EURAM type) with Ar atmosphere was used to avoid that water has contact with air. The sampling and measuring of pH, Eh, electrical conductivity (E.C.), Fe(II) and alkalinity *in situ* was made inside the anoxic glove box to preserve the anoxic conditions of the samples, as described below.

3.1.1. *In situ* measurements

The redox potential and the pH were measured inside the anoxic glove box by means of an ORION 720A pH-meter equipped with a Metrohm 6.0451.100 Pt electrode and a Metrohm 6.0234.100 pH combination electrode. The pH electrode was calibrated at the sample temperature using Merck pH 4 and pH 7 buffer solutions. A redox buffer solution of Fe(CN)₆⁴⁻/Fe(CN)₆³⁻ (10⁻³ M), at $+250 \pm 5$ mV was used for the standardizations of the potential measurements.

Electrical conductivity (EC) was measured using an ORION 115 conductimeter. The conductivity cell was checked/calibrated with a standard solution of 12.6 mS/cm (NaCl) at the same temperature as the sample.

Fe(II) was analyzed using the specific procedure described in Sánchez *et al.* (2004). The determination of the absorbance was performed at 562 nm against a blank using a Spectroquant Vega 400 Merck portable spectrophotometer, equipped with cells of 1 cm light path.

The alkalinity (expressed as mg/L of HCO₃⁻) was analyzed by a potentiometric Titroprocessor Metrohm 716 DMS. The analyses were made by means of a specific Dynamic Equivalence point Titration (DET) method specifically developed for analyzing 2 mL samples (Sánchez *et al.*, 2003).

3.1.2. Sampling procedure

Water samples were collected inside the anoxic box, from the packed-off interval after leading water to seep over several months. All samples were conventionally filtered through 0.45 μ m syringe filters to remove a large amount of particulate material, and collected in polyethylene bottles for complete chemical characterization. Preservation was undertaken according to the constituents under analysis. Ultrapure hydrochloric acid was used to bring the water samples to pH<2 for determinations of Fe(II) at the laboratory. Major cations and trace elements were determined after bringing the samples to pH<2 with 2 vol% of 60% HNO₃. Non-acidified samples were used to determine anion and silica concentrations.

Water and gas samples were collected inside TEDLAR gas sampling bags for chemical and gas analyses. Norbert Jockwer from GRS (Germany) performed the analyses of gases by using a gas chromatograph VARIAN CP 4900.

3.2. Laboratory methods for extracting water (Oligocene-Miocene Spanish Clay)

Pore water samples and analyses were obtained from 7 cores from the borehole S1 drilled in Oligocene-Miocene clays of Spain. The maintenance of the chemical integrity of the samples from *in situ* conditions to laboratory is difficult. In fact, when the samples are analysed in the laboratory, the extent to which water-rock reactions have proceeded depends on the way of collection and conservation of the samples until analyses (Pearson *et al.*, 2003 and references therein). For this reason, as will be shown further on, pore water analyses need to be checked in order to assess if suitable samples and data have been obtained.

In the case of the Oligocene-Miocene Clay, once borehole was drilled, the core samples were isolated from the atmosphere by means of PVC tubes sealed with paraffin to minimize oxidation or degassing, and were stored in a room with high relative humidity and constant temperature until analyses of both rock and pore waters.

The pore water samples were obtained from the cores using the compression of the rock sample technique (*squeezing*), similar to that developed by Peters *et al.* (1992) and Entwistle and Reeder (1993). A detailed description of the method is given elsewhere (Cuevas *et al.* 1997). The compaction chamber is made of type AISI 329 stainless steel (due to high tensile strength and resistance to corrosion) with an internal diameter of 70 mm. It has been designed to allow a one-dimensional compression of the sample (Cuevas *et al.*, 1997; Fernández *et al.*, 2001b) by means of an automatic hydraulic ram operating downwards being the squeezed water expelled into vacuum vials at both top and bottom of the cell (Fig. 10). The pore water of the Oligocene-Miocene Clay was extracted by applying a constant pressure of 64 MPa onto the sample, under laboratory conditions (25°C), and avoiding contact with atmospheric air. The filtration system (0.5 µm stainless steel AISI 316L porous disk in contact with the sample) allows the extraction of interstitial water by drainage at the top and at the bottom of the sample. The main problem of obtaining accurate information on the composition of pore waters based on this technique is a possible water modification due to irreversible oxidation and degassing during the handling of the samples (Pearson and Bath,

2003; Fernández *et al.*, 2003). The accuracy of the pore water chemical data was assessed through charge balance calculations, and geochemical modelling was used to check if the squeezed waters are altered.

Before squeezing, sub-samples of each sample were taken for different physical determinations. The grain density was measured by the pycnometer method. The dry density (ρ_d) of the samples was determined by the mercury displacement method. The gravimetric water content was determined by weighting the sample before and after oven-drying at 150 °C for 24 hours. The moisture content of the individual samples was calculated from the ratio between water weight loss after heating sample to 110 °C for 24 hours, and the weight of the dried clay, expressed as percentage.

The Chapman displacement method was used to determine the exchangeable cations by means of successive washing with 1N ammonium acetate at pH=8.2, after flushing the soluble salts (Thomas, 1982). To determine the cation exchange capacity, the exchange sites of the sample were saturated with sodium by means of successive washing with 1N sodium acetate at pH=8.2. The adsorbed sodium was displaced by successive extractions with ammonium acetate 1N at pH = 8.2 (Rhoades, 1982).

3.3. Analytical techniques in laboratory

Common anions (Cl^- , Br^- , NO_3^- , NO_2^- , PO_4^{3-} , SO_4^{2-}) were analyzed by ion chromatography (Dionex DX-4500i). An ORION 901 microprocessor ion-analyzer, equipped with ion selective electrodes, was used for F^- and I^- determinations. The alkalinity (expressed as mg/L of HCO_3^-) was analyzed by a potentiometric Titroprocessor Metrohm 785. The analyses were made by means of a specific Dynamic Equivalence point Titration (DET) method specifically developed for analyzing 2 mL samples (Sánchez *et al.*, 2003). The main cations and some trace elements were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES), in a Jobin Yvon JY48+JY38 spectrometer. Sodium, lithium and potassium were determined by flame emission spectroscopy in a Perkin Elmer 2280 spectrometer. Trace and ultratrace elements were determined using a Finnigan Mat SOLA quadrupole ICP-MS apparatus. Total silica was determined by the ammonium molybdate colorimetric method using a UV-VIS spectrophotometer (EPA 370.1 Method). The tritium content was determined on 1 L of sample by means of liquid scintillation (LS) spectrometry after electrolytic enrichment in CIEMAT laboratories.

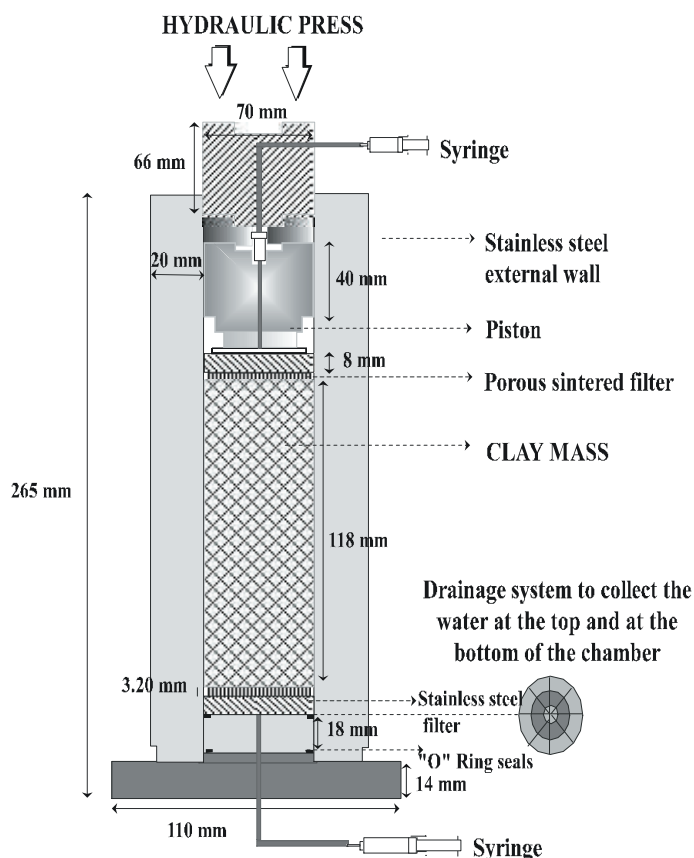


Fig. 10.- Photography and schematic representation of the pore water extraction device from core samples.

Fig. 10.- Fotografía y representación esquemática del equipo utilizado para la extracción del agua intersticial de testigos de sondeo.

3.4. Geochemical modelling

Geochemical modelling was used in this work as a tool to check the representativity of the samples and the analytical data and to interpret and discuss the processes affecting the water chemistry. Further, the physicochemical and compositional reconstruction of the formation pore waters was made.

The geochemical data were interpreted with the geochemical code PHREEQC (Parkhurst and Appelo, 1999) and the WATEQ4F modified thermodynamic database (Ball and Nordstrom, 1991) and NAGRA/PSI thermodynamic database (Hummel *et al.*, 2002).

3.4.1. Checking the representativity of the samples and the analytical data

Different aspects can perturb collection of pore water from clays, both by means of squeezing and from boreholes, causing the water chemistry alteration. Pearson and Bath (2003) and Fernández *et al.* (2003) made an

exhaustive review on the factors that have important effects on the chemistry of a clay formation. Some of these effects are considered to check the logics and the quality of the chemical data obtained and used in this research. These processes are: (1) Uncertainties related to the small amount of water available for analysing, that can bring to analytical errors; (2) mineral oxidation (e.g. sulphide oxidation by intrusion of oxygen in the system) by air contact during drilling, handling of cores, storage, or during squeezing, which should cause decrease of pH and dissolution of minerals such as calcite; (3) Outgassing (or ingassing) of CO₂ if system is exposed to air, affecting pH and calcite saturation state; (4) Contamination by metallic materials (e.g. filters used at the top and bottom of the compaction chamber during squeezing); and (5) Pressure effects of squeezing by increasing the solubility of minerals.

According to the mentioned aspects, a number of criteria can be used based on the analytical data, in order to assess data quality. The criteria employed in this work

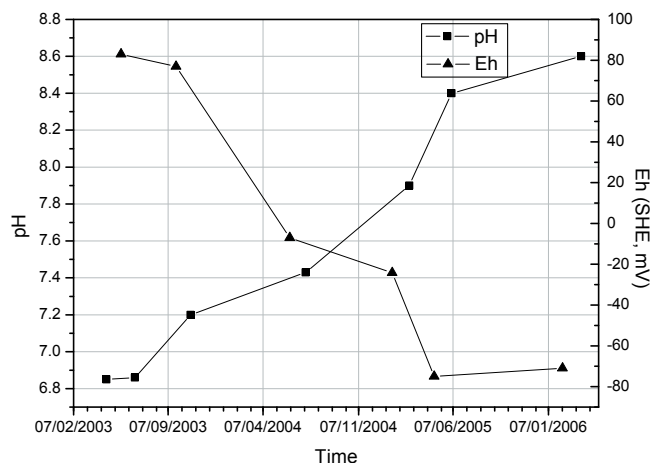


Fig. 11.- pH and redox potential evolution of the pore water samples from borehole BDI-B1 in the different sampling campaigns.

Fig. 11.- Evolución en las medidas de pH y potencial redox de las aguas intersticiales muestreadas en el sondeo BDI-B1 en diferentes campañas de muestreo.

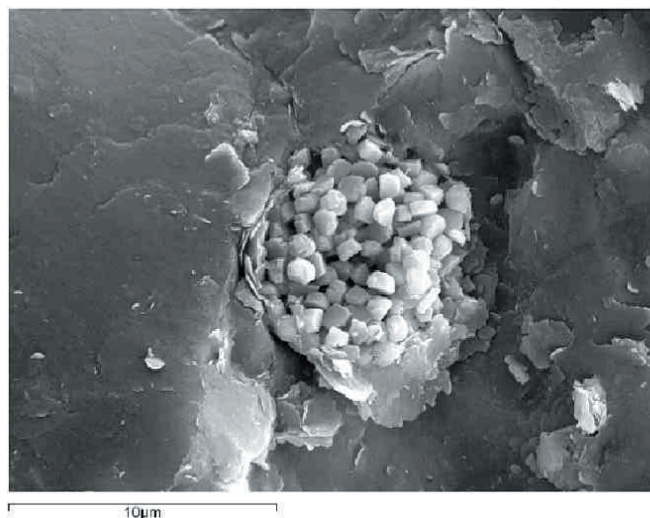


Fig. 12.- SEM microphotograph of the Opalinus Clay showing euhedral pyrite aggregate involved by clays.

Fig. 12.- Fotografía de microscopio electrónico de barrido de la Opalinus Clay en la que se pueden observar agregados euhedrales de pirita envueltos por arcilla.

are: (1) Charge balance calculations as indicator of analytical errors in major components or omission of an ion with significant abundance (Freeze and Cherry, 1979; according to this convention, the error in the charge balance should be <10%); (2) Comparing with existing analyses at other points of the same formation and observing deviation in trends; (3) Anomalous concentration of a solute or anomalous values of pH that might suggest oxidation and/or degassing; it should be interesting to detect the potential impact of CO₂ loss or oxidation as sources of inconsistency in the analytical dataset obtained in situ and/or in the laboratory; (4) Assume, as expected, pore water-rock equilibrium with respect to particular minerals in the clay rock.

Additionally, during the storage period of the core samples for squeezing (case of Oligocene-Miocene Clay) some variations in the saturation degree due to evaporation could occur. If so, exchange with O₂ and CO₂ from atmosphere should be checked. This effect was also evaluated.

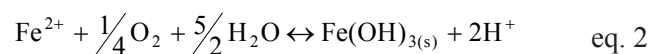
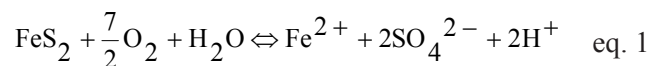
4. Results and discussion

4.1. Water chemistry of Opalinus Clay from borehole BDI-B1

With the downhole equipment described above and the system completely closed to the atmosphere, borehole samples were collected periodically from 2003 to 2006. Hydraulic conductivities were measured in the sampling interval for this time and an average value in the range

of 10⁻¹⁴ m/s was obtained (Fernández *et al.*, 2006), which is somewhat similar to that measured by Marschall *et al.* (2004) as average value for the Opalinus Clay matrix. Table 2 summarizes the data on physicochemical parameters and chemical analyses of the water in various campaigns during this period. The charge balances agreed within less than 10% in all the samples. The water is of sodium-chloride type, with high concentrations of sulphate, calcium and magnesium. The ionic strength is around 0.4 mol/L and the electrical conductivity is 28.7 ± 3.4 mS/cm.

In situ Eh and pH values versus time are presented in figure 11. A trend of increasing pH and decreasing Eh with time can be observed. This evolution is attributed to a tendency towards the stabilization of the system, starting from the borehole drilling to its complete isolation and recovering to the original conditions, with the packer system. During the first stages oxygen entered the borehole and, consequently, the pyrite present in the Opalinus Clay (e.g. Fig. 12) was oxidized, which can be described according to the following reactions:



During the first campaigns a slightly reddish colour was observed in the water samples, which was attributed to the precipitation of iron oxy-hydroxides, according to the described processes, as also observed in other boreholes previously (Gaucher *et al.*, 2003). In fact, calculations

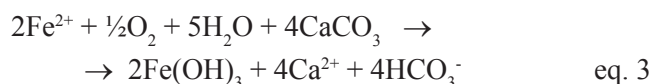
Sampling Date	April 2003	June 2003	October 2003	July 2004	March 2005	June 2005	March 2006
Electrical Cond (mS/cm)	29.8	26.8	28.1	24.3	26.2	31.8	34.3
pH in situ	n.d.	6.8	6.9	7.0	7.6	8.4	8.6
pH lab	7.3	7.5	7.4	7.6	7.6	8.0	7.9
Electrical Neutrality (%)	3.17	-0.90	3.32	-5.75	-4.76	-5.06	1.42
Ionic Strength (M)	0.42	0.43	0.40	0.43	0.39	0.40	0.40
Eh in situ (mV)	n.d.	83	77	-7	-24.2	-75	-71
Tritium (T.U.)	3.82	1.93	n.d.	< 0.7	n.d.	n.d.	n.d.
F ⁻ (mg/L)	0.30	0.30	0.30	0.19	0.51	0.90	0.96
I ⁻ (mg/L)	2.2	2.2	1.8	2.0	2.6	n.d.	n.d.
NH ₄ ⁺ (mg/L)	14.2	12.7	14.0	13.0	13.0	11.0	n.d.
Br (mg/L)	31	28	28	19	22	21	31
Cl ⁻ (mg/L)	11000	12000	11000	13000	11800	12100	10500
NO ₃ ⁻ (mg/L)	< 1	< 1	< 1	< 1	< 1	< 1	< 1
SO ₄ ²⁻ (mg/L)	2100	1833	1700	1700	1600	1700	1600
Alkalinity in situ (mg/L)	n.d.	334	n.d.	n.d.	299	175	214
Alkalinity in lab (mg/L)	344	347	313	303	280	161	253
Fe Total (mg/L)	2.2	4.3	4.1	3.3	1.3	1.9	0.7
Fe(II) in situ (mg/L)	n.d.	1.6	n.d.	n.d.	1.3	n.d.	1.86
Fe(II) in lab (mg/L)	1.3	1.6	1.0	3.1	1.2	1.9	1.0
SiO ₂ (mg/L)	7.4	9.2	4.2	5.8	8.3	14.2	7.5
K (mg/L)	88	89	93	73	80	69	65
Al (mg/L)	0.1	0.1	0.1	0.12	< 0.05	< 0.25	0.10
Li (mg/L)	0.8	0.8	n.d.	n.d.	n.d.	n.d.	n.d.
B (mg/L)	0.1	3.5	3.1	3.0	2.5	3.6	3.2
Ca (mg/L)	922	1033	886	880	806	629	772
Mg (mg/L)	611	574	456	505	395	545	449
Na (mg/L)	6480	6300	6650	6300	6000	6100	6100
Sr (mg/L)	43	40	41	36	37	40	34
Mn (mg/L)	0.4	0.3	0.3	0.22	0.12	0.25	0.18
Saturation index _{calcite}	0.19	0.32	0.27	0.33	0.87	1.22	1.66
log pCO ₂	-1.45	-1.52	-1.59	-1.69	-2.35	-3.49	-3.55

Table 2.- Physicochemical parameters and chemical and isotopic composition of the pore waters extracted from borehole BDI-B1.

Tabla 2.- Parámetros fisicoquímicos y composición química e isotópica del agua intersticial extraída del sondeo BDI-B1

of saturation indices for Fe(OH)₃ indicate oversaturation with respect to this mineral. In this respect it is noteworthy that in the last sampling campaign all the iron measured was Fe(II), but that was not the case for the first sampling campaigns, when oxygen was present in the borehole, and part of the iron was Fe(III) (see Table 2).

The oxidation led to an acidification, which was neutralized by the pH buffering of the carbonates, according to the reaction:



Indeed, the higher alkalinities are measured in the first sampling campaigns (Table 2) and trend to decrease with time, as well as the calcium concentration.

The sulphate concentration (Table 2) reflects also the oxidation process during the first stages. Figure 13 depicts the variation of pH and SO₄²⁻ with time. There is a good correlation between the low pH and the high concentra-

tion of sulphate due to pyrite oxidation, which causes H⁺ and SO₄²⁻ release (see eq. 1).

The evidences of exchange of oxygen with the atmosphere (oxidation) during the first sampling campaigns might also lead to think in an additional effect of exchange of CO₂ (outgassing or ingassing). The calculations of pCO₂ (based on the measured values for pH and alkalinity) are in Table 2. A decrease of the pCO₂ regarding that calculated by means of modeling by Pearson *et al.* (2003) for the Opalinus Clay, at the closest point to BDI-B1 (pCO₂ < 10⁻³ bar), should confirm an exchange of CO₂. Indeed, this progressive decreasing of pCO₂ is correlated with precipitation of carbonate, as shown in Table 2 (strongly oversaturation with respect to calcite is observed).

Up to now the pCO₂ values for Opalinus Clay were obtained from calculations by using the in situ measurements of pH and alkalinity at different points in the formation, or pH and alkalinity measured from pore water

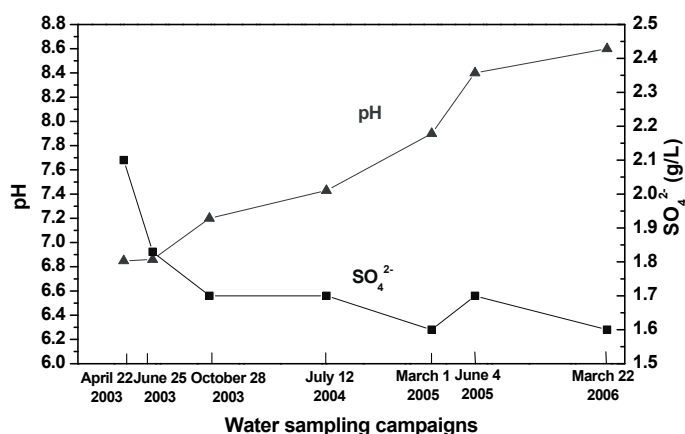


Fig. 13.- pH and SO_4^{2-} evolution in the different sampling campaigns of borehole BDI-B1.

Fig. 13.- Evolución del pH y de la concentración de sulfato en las diferentes campañas de muestreo del sondeo BDI-B1.

extracted by squeezing of cores, assuming alkalinity equal to HCO_3^- . The interpretation of the calculated $p\text{CO}_2$ values was based in certain statements: on one hand, $p\text{CO}_2 \geq 10^{-3.5}$ could be representative of the formation water and lower values (mainly those obtained from squeezing data) are attributed to interaction with the atmosphere during the storage of the cores before being analysed (Pearson *et al.*, 2003).

Therefore, there are some uncertainties linked to the interpretation of the carbonate system. The dataset corresponding to the last sampling campaign in borehole BDI-B1 included CO_2 measurements from samples taken inside the anoxic box in Tedlar gas sampling bags. The measured $p\text{CO}_2$ is $10^{-1.9}$ bar, which is in disagreement with the calculations made for this campaign by means of modeling, based on the in situ measured values for pH and alkalinity (see Table 2, $p\text{CO}_2 = 10^{-3.55}$).

The discrepancies can be explained in different ways: (1) The *in situ* pH measurements tend to increase with time, which could reflect a continuous CO_2 degassing, and the water would tend to equilibrate via calcite precipitation; (2) Microbial activity was detected in studies made on this borehole (Mauclaire and McKenzie, 2006). It is an important source of CO_2 according to $\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2$, and should contribute to the increase of CO_2 observed from the measurements made from samples taken in the anoxic globe box. The reason for the calcite precipitation could be linked to the production of CO_2 in the sampling sections by microbial activity and a later degassing during sampling; (3) The alkalinity values measured in situ and at CIEMAT's laboratory are in rather good agreement (Fig. 14). It is logic considering that the alkalinity measurements are independent of outgassing, unless carbonate precipitates. While degassing of CO_2 could

not contribute to alter the alkalinity, the presence of microbial activity could have affected, as investigated by Eichinger and Wersin (2004), Wersin *et al.* (2004) and Mauclaire and McKenzie (2006) for the long-term pore water experiment at Mont Terri.

Each of these aspects could mislead the interpretation of the carbonate system and it is difficult to evaluate specific contributions to the alteration, so there are still a number of uncertainties in the parameters related with the carbonate system.

The Br/Cl^- and $\text{SO}_4^{2-}/\text{Cl}^-$ ratios were compared with those found in other water sampling experiments at Mont Terri (Degueldre *et al.*, 2003; Pearson *et al.*, 2003). These ratios are close to the seawater, as in all the Opalinus clay water analysed (Fig. 15), although depend on the location of water sampled within the Opalinus Clay formation (e.g. the proximity to the surrounding aquifers).

A Br/Cl^- ratio similar to that of seawater, suggests a syngenetic marine origin of the water (Bath and Gautschi, 2003). On the other hand, the observed chloride and bromide concentrations are lower than the seawater values (~half of the seawater values). The infiltration of meteoric waters could have induced the dilution of the ancient Opalinus Clay pore water. Uplift and erosion during the Pliocene/Quaternary initiated the influx of meteoric water to the sequence (Bossart and Wermeille, 2003). Infiltration to the Liassic limestone would have started in the Quaternary, around 350 thousand years ago. Groundwater flow would have been redirected northwards by the low permeability of the Opalinus Clay (Bath and Gautschi, 2003). Nevertheless, the lower content of the conservative elements seems to be related to a diffusion mechanism from the Opalinus Clay towards the overlying (Lower Dogger limestone) and underlying formations (Jurensis Marls). The chloride and sodium concentration versus the location of the boreholes in the underground laboratory in a NW-SE profile depicts a trend that seems to indicate an effect of solute out-diffusion, specially towards the most permeable overlying Dogger limestones (see in Fig. 3 the chloride trend). The Lower Dogger is a recharge and karstic zone containing dilute meteoric water, which establishes a chemical gradient in relation to the clay formation with high saline contents. This leads to a long-term large-scale process of mass transfer by diffusion (Arcos *et al.*, 2001; Degueldre *et al.*, 2003; Pearson *et al.*, 2003).

4.2. Water chemistry of Oligocene-Miocene Clay from borehole cores

The composition of all the pore waters collected by squeezing is given in Table 3. In all the samples analyzed,

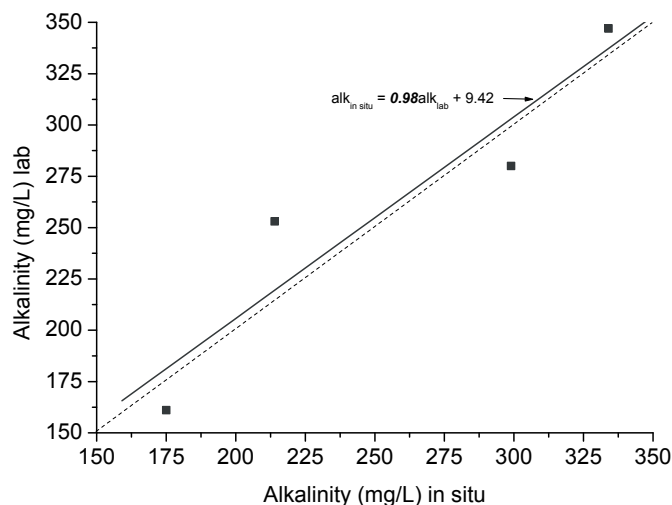


Fig. 14.- Diagram showing the *in situ* alkalinity measurements versus the laboratory alkalinity measurements.

Fig. 14.- Diagrama en el que se muestran las medidas de alcalinidad medidas *in situ* versus las medidas en el laboratorio.

charge balances were better than 10%, thus analytical errors can be discarded. Most of the waters are sodium-sulphate type waters, with high concentration of chloride, calcium and magnesium. According to Hanor (1987) the waters can be classified as brackish (TDS ranging from 1000 to 10000 mg/L). pH values range from neutral to slightly alkaline (6.9 to 8.1). The ionic strength is around 0.2 mol/L for all the samples and the electrical conductivity varies from 7.9 to 13.7 mS/cm. The total cation exchange capacity ranges from 16 to 49 meq/100g, being the exchangeable cation population dominated by calcium and sodium (Table 4).

As factors that might have contributed to the alteration of the samples the following were considered: (1) the conservation and storage of the samples and, for instance, the degree of atmosphere isolation; and (2) the handling of the samples before squeezing and during analysis.

Table 5 shows a number of parameters used to check if the results are indicative of the *in situ* geochemical conditions of the formation. Some of them, such as saturation indices and $p\text{CO}_2$ were calculated from the analytical data, with the geochemical code PHREEQC. Each sample was checked separately. Notice that there is no data on *in situ* pore water extracted from boreholes to compare with.

In core sample C201 and C205 the values of pH, $p\text{CO}_2$ and saturation index with respect to calcite do not seem indicate any anomaly.

The water degree of saturation calculated for core sample C203 is the lowest ($S_r = 0.62$), which may indicate evaporation during the storage. The pH, $p\text{CO}_2$ and saturation index with respect to calcite indicate a slight CO_2 outgassing.

In core sample C253 the values of pH, $p\text{CO}_2$ and saturation index with respect to calcite indicate an oxidation process. The B content is high as well, which could affect the alkalinity by overestimation of the inorganic carbon concentration. This should reduce even more the saturation index of calcite, so it should not discard the oxidation process.

Regarding the core sample C257, the data indicate that this sample is oversaturated with respect to calcite. The pH and $p\text{CO}_2$ values reflect CO_2 outgassing.

The pore water extracted from core sample C283 has the lower pH and the highest $p\text{CO}_2$, alkalinity and sulphate concentration. This sample is slightly oversaturated with respect to gypsum, so it seems to reflect an oxidation process of pyrite. However, there is oversaturation regarding the calcite and the $\text{SO}_4^{2-}/\text{Cl}^-$ is the lowest, which is in contradiction with pyrite oxidation. To evaluate the possible oxidation process of this sample geochemical modeling was used. A kinetic process of pyrite oxidation, maintaining calcite equilibrium was assumed. For that, the Singer and Stumm (1970) model was applied. It considers the oxidation rate of pyrite controlled by the oxidation of Fe(II) to Fe(III) according to:

$$\frac{dm_{\text{Fe}^{2+}}}{dt} = -\left(2.91 \times 10^{-9} + 1.33 \times 10^{12} * a_{\text{OH}^-}^2 * P_{\text{O}_2}\right) * m_{\text{Fe}^{2+}} \quad \text{eq. 4}$$

where t is time (s), a_{OH^-} is the hydroxide activity, $m_{\text{Fe}^{2+}}$ is the molality of the ferrous iron in the solution and P_{O_2} is the oxygen partial pressure (atm). The precipitation of amorphous ferric iron was assumed. The result is similar to the measured one, so the sample is considered unaltered. The higher sulphate content could be just related with the sedimentation environment, which is different to the samples analyzed above, more than with artifacts during sampling or analyses.

In the core sample C290 the pore water has the highest pH and a $p\text{CO}_2$ similar to the atmospheric one. The alkalinity is the lowest and the sample is oversaturated regarding the calcite. This points to CO_2 outgassing. On the other hand, the iron and zinc concentration are quite anomalous compared with the other samples. It could be associated to a metallic contamination by filters or pressure effects when squeezing, since the pressure increases the solubility of minerals, affecting the mineral-solution equilibria (Fernández *et al.*, 2003).

There are no data on redox potential for any sample and the confidence for measured iron concentrations is low due to the mentioned evidences on oxidation processes and contamination. There is some correlation between the variations in the $\delta^{34}\text{S}$ content and the variations in the sulphate concentration and organic matter content of the cores (Table 6). This fact can be interpreted as sulphur

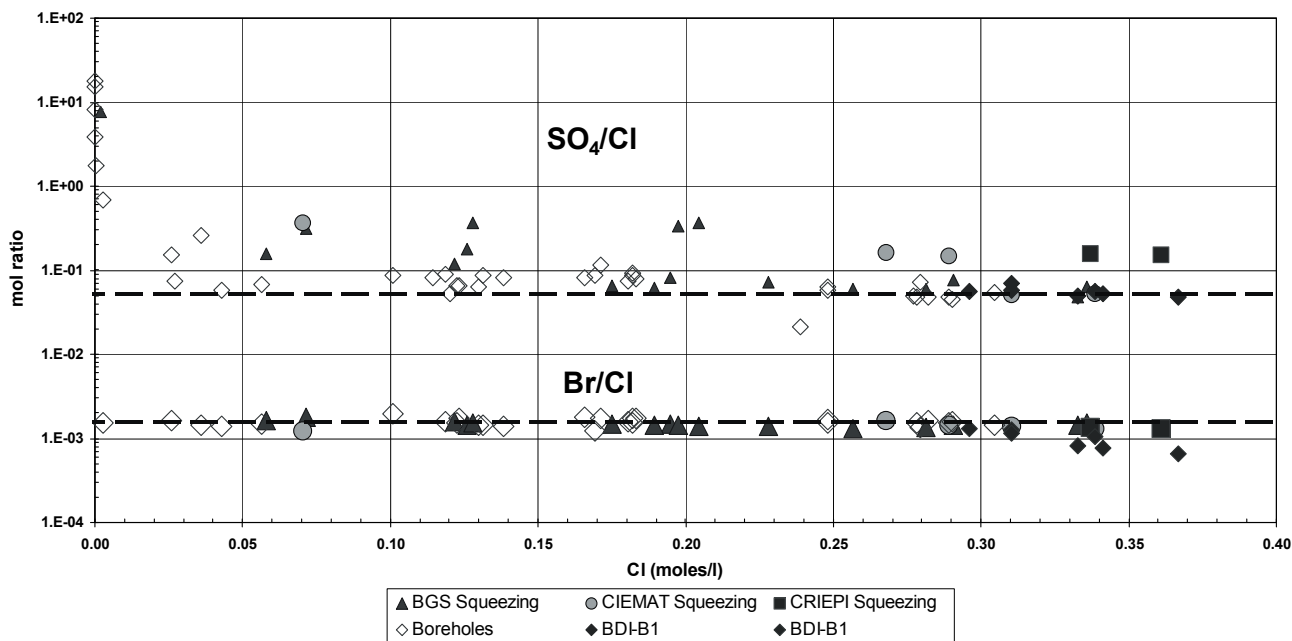


Fig. 15.- $\text{SO}_4^{2-}/\text{Cl}^-$ and Br^-/Cl^- ratios plotted against Cl concentrations of boreholes and squeezed water samples from Opalinus Clay. Dashed lines represent molar ratios in seawater (seawater molar ratios: $\text{SO}_4^{2-}/\text{Cl}^- = 5 \cdot 10^{-2}$ and $\text{Br}^-/\text{Cl}^- = 1.5 \cdot 10^{-3}$) (modified from Pearson *et al.*, 2003).

Fig. 15.- Relaciones $\text{SO}_4^{2-}/\text{Cl}^-$ y Br^-/Cl^- frente a la concentración de cloruros de las muestras de agua intersticial procedente de los sondeos y del agua extraída por compresión de los testigos de la Opalinus Clay. Las líneas discontinuas representan las relaciones molares en el agua del mar ($\text{SO}_4^{2-}/\text{Cl}^- = 5 \cdot 10^{-2}$ and $\text{Br}^-/\text{Cl}^- = 1.5 \cdot 10^{-3}$) (modificado de Pearson *et al.*, 2003).

oxidation/reduction processes, the latest microbially-mediated, which control the redox in the system (e.g. Fig. 16).

4.2.1. Synthesis of assumed geochemical processes

Geochemical equilibrium calculations performed from the present formation pore water compositions indicated that the sampled pore water closely approaches saturation with respect to the sulphate minerals celestite, anhydrite, gypsum and barite. Since the water degree of saturation is lower than 1 in all the samples (Table 5) an evaporation process, with exchange of O_2 and CO_2 , might occur. An oxidation process by the supply of atmospheric oxygen into the samples during the storage period might have led to the sulphide oxidation. In such a case, the system exchanged not only O_2 but also CO_2 with the atmosphere, and sulphide and Fe^{2+} were oxidized to sulphate and Fe^{3+} , precipitated as $\text{Fe}(\text{OH})_3$ (oversaturated as indicated in the calculations made with PHREEQC). These hypothesis were considered in terms of modelling.

Calcium required for gypsum precipitation was assumed to be present from cation exchange and calcite dissolution, the last triggered by the H^+ produced by pyrite oxidation, buffering this acid production.

Furthermore, carbonate minerals analyses indicate that these minerals are being dissolved because of pore water-undersaturated conditions; SEM studies provided evi-

dences on calcite partially dissolved and with corroded edges.

The excess of sodium concentration with respect to chloride was attributed to cation exchange processes. High potassium concentrations might be derived from silicates transformation and equilibrium with the exchanger population. Magnesium is consumed in the process of chlorite formation (there is a positive correlation between $[\text{Mg}]$ and % wt. of chlorite). Calcium is controlled by calcite dissolution and cation exchange.

4.2.2. Reconstructing the pore water composition

It is assumed that the pore water composition represents meteoric water contained in the sediments at the time of deposition, evolved until the present by diagenetic water-rock reactions and diffusive transport, and modified in terms of evaporation, as a consequence of storage and handling of samples.

The geochemical modeling used is a simple equilibrium modelling of aqueous species and water-rock reactions. It is thought that the pore water chemistry is controlled by chemical equilibrium with respect to most of the reactive minerals contributing to the water-rock interaction processes in the clay formation, with the exception of certain free or non-reacting constituents. This seems reasonable from various constraints such as the fine-grained natu-

Squeezed Sample	C 201	C 203	C 205	C 253	C 257	C 283	C 290
Depth (m)	197	199	202	249	253	278	286
Humidity (%)	19,9	18,4	24,4	15,5	20,9	11,4	14,2
Vol extracted (mL)	76	31,7	74,85	38	84,9	---	22
pH	7,53	7,88	7,65	7,17	7,72	6,90	8,13
Electrical Cond (mS/cm)	11.7	11.6	13.7	14.6	13.7	---	---
Ionic Strength (M)	0,221	0,231	0,219	0,238	0,229	0,296	0,274
Electrical Neutrality (%)	-0,68	5,12	0,59	-4,25	8,77	0,98	2,61
Cl ⁻ (mg/L)	940	1030	940	1100	899	2200	1600
SO ₄ ²⁻ (mg/L)	7700	7800	7500	8200	7400	9300	9000
Br ⁻ (mg/L)	<1	<1	<1	<1	<1	<1	<1
NO ₃ ⁻ (mg/L)	2,5	1	<1	1,3	2,1	1,7	<1
Alkalinity (mg/L)	89	152,72	123	110	252	410	66
F ⁻ (mg/L)	<1	<1	2,1	<1	<1	---	---
I ⁻ (mg/L)	0,675	17	16	1,9	---	---	---
SiO ₂ (mg/L)	12,7	---	15,4	12,8	22	---	---
Al (mg/L)	<0,002	0,081	0,0047	0,94	0,0022	0,188	<0,2
Ca (mg/L)	425	470	375	385	440	870	755
Mg (mg/L)	400	540	390	265	345	480	370
Na (mg/L)	3000	3250	3100	3400	3700	4200	4000
K (mg/L)	65	---	32	32	19	35	32
Sr (mg/L)	7,9	9,3	7,3	9,0	8,4	17	11
Li (mg/L)	0,89	---	0,041	2,2	0,043	---	---
B (mg/L)	0,78	1,1	0,90	21	1,4	<0,3	0,64
Ba (mg/L)	<0,06	0,10	0,08	<0,3	0,09	<0,11	<0,1
Fe Total (mg/L)	0,09	0,08	<0,5	<0,5	0,2	0,34	123
Fe(II) (mg/L)	<0,5	<0,5	<0,5	<0,5	<0,2	---	33,2
Mn (mg/L)	0,28	0,17	0,12	<0,3	0,25	1,8	1,2

Table 3.- Physicochemical parameters and chemical composition of the pore waters extracted by squeezing from Oligocene-Miocene Clay cores from borehole S1.

Tabla 3.- Parámetros fisicoquímicos y composición química del agua intersticial extraída de los testigos del sondeo S1 de la arcilla del Oligoceno-Mioceno.

Sample	Depth (m)	Al ³⁺	Ca ²⁺	Mg ²⁺	Na ⁺	Sr ²⁺	K ⁺	Ba ²⁺	Mn ²⁺	Fe ³⁺	CEC
C201	197	0.03	10.53	7.61	7.61	0.13	1.28	0.02	---	0.01	27
C203	199	---	15.18	6.38	5.44	0.09	1.15	0.04	---	---	28
C205	202	---	20.04	4.94	3.59	0.27	1.60	0.02	---	---	30
C253	249	0.09	11.73	4.11	4.89	0.06	1.92	0.08	---	0.03	23
C257	253	---	14.30	4.32	5.98	0.06	1.41	0.03	---	---	26
C283	278	---	13.71	3.50	4.35	0.06	1.15	0.07	0.005	---	23
C290	286	0.02	12.38	2.06	3.48	0.03	1.60	0.03	0.005	---	20

Table 4.- Sum of the exchangeable cations and exchange population analyzed from Oligocene-Miocene Clay cores from borehole S1.

Tabla 4.- Capacidad total de intercambio catiónico y cationes de cambio analizados en los testigos del sondeo S1 de la arcilla del Oligoceno-Mioceno.

re of the Oligocene-Miocene Clay, assuming a long residence time of the pore water within the rock, inferred by isotopic studies on carbonates and gypsum, and petrography evidence from minerals such as calcite, dolomite, gypsum, pyrite and iron hydroxides, suggesting that they are the main reactive phases.

For applying corrections based on water-rock interaction processes, exchange with atmospheric gases, and

ionic exchange, all the data obtained by means of squeezing were considered. The aim was to correct the processes occurred in the sample due to storage and handling. The corrections were made following different steps: (1) Estimate the humidity of the samples by assuming a complete water saturation degree, to rectify the evaporation effect; and (2) Correct the composition of the water considering equilibrium with the minerals present in the

formation, the interaction with atmosphere gases, ionic exchange processes and water-rock reactions during storage and handling of samples.

(1) The humidity assuming complete water saturation of samples was calculated from:

$$w_{S_r=1} = \frac{\left(\frac{p.e. - \rho_d}{p.e.} \right)}{\rho_d} = \frac{n}{\rho_d} \left(\frac{L}{Kg} \right) \quad \text{eq. 5}$$

where w is the humidity, ρ_d dry density, n is porosity and $p.e.$ is the specific weight or particle density (Table 7). Then, the volume of water lost by evaporation was calculated as:

$$V_{\text{evap}} \left(\frac{L_{\text{water}}}{Kg_{\text{clay}}} \right) = (w_{S_r=1} - w) \quad \text{eq. 6}$$

$w_{S_r=1}/w$ means the quantity of water necessary to achieve the complete saturation, by unity of water volume, assuming that water density is 1 g/cm³. Table 7 shows the results. So, the corrections to the chemical composition of the pore water, were made by adding V_{evap} to the solution following the equation 6:

$$H_2O_{\text{added}} = 55,5 \times (w_{S_r=1} - w) \times w^{-1} = 55,5 \times \left(\frac{w_{S_r=1}}{w} - 1 \right) \left(\frac{mol_{\text{water}}}{L_{\text{solution}}} \right) \quad \text{eq. 7}$$

where w^{-1} is the coefficient used to recalculate the water added from mol/kg_{clay} to mol/kg_{solution}.

(2) If evaporation affected to the solid phases (e.g. pyrite and calcite) and the exchange population of the clayey fraction, the equilibrium of the solution with respect to these minerals and the exchange population should be considered. The calculations of the redox potential were made considering that in the lower unit the redox is controlled by the equilibrium between the iron measured in the solution and the mineral phase Fe(OH)₃; and in the upper unit the redox is controlled by the equilibrium gypsum/pyrite (S(VI)/S(-II)).

The results are shown in Table 8. The pH in all the samples is around 7.6 (except in sample 283) and the average pe is around -3.5. Calcium, from calcite dissolution, contributes to the modification of the cation exchanger population in the clay and to the cation composition of the pore water.

4.2.3. Modelling the redox evolution of the system

This section presents an example of the redox calculations made with the sample C201. Some slow kinetic processes, such as organic matter degradation, are difficult to adjust to equilibrium. Because the clay formation is rich in organic matter (0.7 - 4.1 weight percent C), it was assumed that the redox system could be controlled

Sample	C201	C203	C205	C253	C257	C283	C290
SO ₄ ²⁻ /Cl ⁻	3.03	2.80	2.95	2.75	3.04	1.56	2.08
pH	7.53	7.88	7.65	7.17	7.72	6.90	8.13
Calculated log pCO ₂	-2.72	-2.86	-2.70	-2.29	-2.46	-1.44	-3.50
Electrical Neutrality (%)	-0.68	5.12	0.59	-4.25	8.77	0.98	2.61
Humidity (%)	19.9	18.4	24.4	15.5	20.9	11.4	14.2
Ionic Strength (M)	0.22	0.23	0.22	0.24	0.23	0.30	0.27
Water Saturation Degree	0.88	0.62	0.85	0.95	0.91	0.88	0.91
Ca (mol/L)	1.06x10 ⁻²	1.17x10 ⁻²	9.36x10 ⁻³	9.61x10 ⁻³	1.10x10 ⁻²	2.17x10 ⁻²	1.88x10 ⁻²
Mg (mol/L)	1.65x10 ⁻²	2.22x10 ⁻²	1.60x10 ⁻²	1.09x10 ⁻²	1.42x10 ⁻²	1.97x10 ⁻²	1.52x10 ⁻²
Alkalinity	89	153	123	110	252	410	66
SO ₄ ²⁻ (mol/L)	8.02x10 ⁻²	8.13x10 ⁻²	7.81x10 ⁻²	8.54x10 ⁻²	7.71x10 ⁻²	9.69x10 ⁻²	9.38x10 ⁻²
Mg/Ca	1.55	1.89	1.71	1.13	1.29	0.91	0.81
Fe (mol/L)	1.61x10 ⁻⁶	1.43x10 ⁻⁶	-	-	3.58x10 ⁻⁶	6.09x10 ⁻⁶	2.20x10 ⁻³
Fe(II) (mol/L)	-	-	-	-	-	-	5.94x10 ⁻⁴
pe Fe(II)/Fe(III)	-	-	-	-	-	-	1.49
Zn (mg/L)	0.4	0.4	0.8	1.4	0.9	3.8	16.0
B (mg/L)	0.8	1.1	0.9	21.0	1.4	-	0.6
Saturation Index _{dolomite}	0.11	1.42	0.57	-0.74	1.35	0.51	1.14
Saturation Index _{calcite}	-0.09	0.52	0.11	-0.45	0.56	0.22	0.56
Saturation Index _{gypsum}	0.02	0.05	-0.04	-0.01	0.01	0.31	0.27
Saturation Index _{anhydrite}	-0.20	-0.17	-0.26	-0.23	-0.20	0.10	0.05

Table 5.- Parameters considered to check the representativity of the samples and the analytical data obtained from the Oligocene-Miocene Clay cores.

Tabla 5.- Parámetros considerados para valorar la representatividad de las muestras y de los datos analíticos obtenidos de los testigos de la arcilla del Oligoceno-Mioceno.

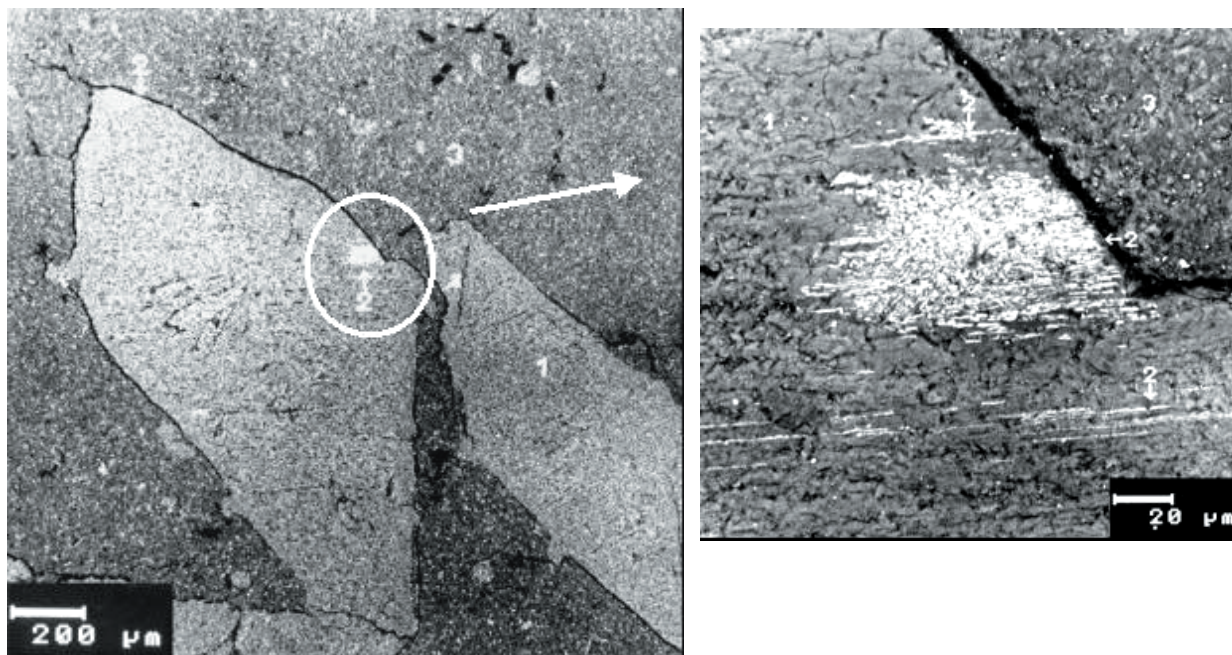


Fig. 16.- SEM photomicrograph of the Oligocene-Miocene Clay. Precipitation of pyrite (2) is observed along exfoliation planes of gypsum (1) in the vicinity of micrite (3) where organic matter is probably hosted. This texture may be indicative of sulfate reduction (Peña *et al.*, 2003).

Fig. 16.- Fotografía con microscopio electrónico de barrido de la arcilla del Oligoceno-Mioceno. Se observa precipitación de pirita (2) a favor de los planos de exfoliación del yeso (1) en las proximidades de micrita (3) donde probablemente esté alojada materia orgánica. Esta textura puede estar indicando un proceso de reducción de sulfatos (Peña *et al.*, 2003).

by the kinetics of microbially-mediated degradation reactions of organic matter.

In this sense, there is some evidence of the occurrence of sulphate reduction in the system (e.g. Fig. 16). Moreover, analysis of the $\delta^{34}\text{S}$ of gypsum compared with the sulphate concentrations measured in pore water and the chemical composition of the clay indicates two different zones (upper and lower zone, as defined in section 2.2.). The presence of two zones is further confirmed by a correlation between enriched $\delta^{34}\text{S}$ in gypsum, lower sulphate concentration in pore water, and higher ferrous iron concentrations in the upper zone of the clay with respect to the lower one, which clearly indicate the presence of sulphate reduction (Table 6). After these initial considerations, the PHREEQC geochemical code was used to simulate the evolution of the redox system.

Once demonstrated that alteration of the samples from *in situ* to laboratory conditions occurred and a long storage period lead to the exchange with atmospheric oxygen and CO_2 a modelling exercise, selecting sample C201, considered to be initial pore water in equilibrium with atmospheric oxygen, was made. The simulation starts in equilibrium with calcite, used to correct for the degassing of CO_2 , and with dolomite, gypsum, and ferrihydrite.

The rate of oxidation of pyrite is based on the rate law from Williamson and Rimstidt (1994):

$$r = 10^{-8.19} \frac{m_{\text{DO}}^{0.5}}{m_{\text{H}^+}^{0.11}} \quad \text{eq. 8}$$

where r is the rate of pyrite dissolution in $\text{mol m}^{-2}\text{s}^{-1}$. Equilibrium was used for precipitation of pyrite.

The formulation for microbially-mediated degradation of organic matter was based on a Monod approach with only electron acceptor limitation. The following rate expression was used:

$$r = r_{\text{max}} \left(\frac{C}{K_m + C} \right) \quad \text{eq. 9}$$

where r is the rate of organic matter degradation in $\text{mol m}^{-2}\text{s}^{-1}$, r_{max} is the maximum reaction rate, K_m is the half-saturation constant for electron acceptor and C is the concentration of electron acceptor. Only aerobic respiration and sulphate reduction were considered as degradation processes.

Figure 17 illustrates the evolution of p_e in a time period of 105 years. Four different periods, with changes in the redox controlling species can be described. The first one is controlled by the pair $\text{O}(-\text{II})/\text{O}(0)$. Pyrite oxidation and resulting ferrihydrite precipitation, together with processes such as organic matter degradation by aerobic respiration (until pore water is depleted in dissolved oxygen) and sulphate reduction, guide the next step in the redox evolution.

Sample	Unit	Depth (m)	Sulphate (mg/L)	$\delta^{34}\text{S}_{\text{gypsum}}$ (‰)	FeO (wt.%)	$\text{CO}_{2\text{org}}$ (wt.%)
C201	Upper	197	7700	12.9	0.80	4.12
C203	Upper	199	7800	---	0.94	0.90
C205	Upper	202	7500	12.9	0.93	2.20
C253	Upper	249	8200	---	0.98	0.80
C257	Upper	253	7400	12.8	0.94	0.71
C283	Lower	278	9300	---	0.74	0.90
C290	Lower	286	9000	8.5	0.66	1.82

Table 6.- Chemical and isotopic results considered to analyze the evolution of the redox system in the Oligocene-Miocene Clay.

Tabla 6.- Resultados químicos e isotópicos considerados para analizar la evolución del sistema redox en la arcilla del Oligoceno-Mioceno.

Sample	Depth (m)	w (%)	ρ_d (g/cm ³)	S_r	n	$w_{\text{sr}=1}$	$w_{\text{sr}=1}/w$
C201	197	20.4	1.69	0.88	0.39	23.08	1.13
C203	199	11.8	1.81	0.62	0.35	19.17	1.62
C205	202	19.4	1.70	0.85	0.39	22.71	1.17
C253	249	14.9	1.93	0.95	0.30	15.70	1.05
C257	253	18.3	1.78	0.91	0.36	20.06	1.10
C283	278	12.6	1.98	0.88	0.29	14.39	1.14
C290	286	13.3	1.97	0.91	0.29	14.67	1.10

Table 7.- Physical parameters to calculate the humidity for the Oligocene-Miocene Clay assuming that samples are completely saturated.

Table 7.- Parámetros físicos para calcular la humedad de las muestras de la arcilla del Oligoceno-Mioceno suponiendo que están completamente saturadas.

Once dissolved oxygen is almost completely consumed, only sulphate reduction controls the redox evolution as a non-equilibrium process. In this stage, the redox condition is regulated by the Fe(II)/ferrihydrite pair. When complete reductive dissolution of previously formed ferrihydrite is achieved, dissolution of gypsum and precipitation of pyrite starts. Because the solution is depleted in iron and no reasonable iron source in the solid is found, the SO_4/HS^- pair is likely to buffer the latest redox state of the system.

5. Comparison of pore water chemistry of different mudrocks

A comparison on pore water chemistry at different locations (e.g. Opalinus Clay and Oligocene-Miocene Clay (this work), and Boom Clay from Belgium (Dierckx, 1997) and Callovo-Oxfordin Clay from France (Andra, 2005) have been made. The differences between the water chemical composition are well observable in the Schoeller's diagram shown in figure 18, which illustrates the pattern of the total concentration of major ions of the pore waters. All the waters have rather high salinity, being sulfate and chloride the dominant anions, except for the Boom Clay. However, the graph shows that the main

differences are expressed in the contents of sulfates and bicarbonates, suggesting that processes related to carbonate and redox systems are critical in defining the composition of these waters. As shown for Opalinus Clay and Oligocene-Miocene Clay the variations can be explained by principles of chemical equilibrium and cation exchange. Although the origin itself of the waters is different for both clays, chemical perturbations (e.g. oxidation and/or CO_2 exchange) induce the same response, with a tendency of the system to recover the "unperturbed state". In this sense, the geochemical model considered for each individual system assumes that the equilibrium of "key minerals" commonly present in these mudrocks, such as calcite, siderite, pyrite, and chalcedony, and the cation exchange processes, are enough to explain the nature of the pore waters.

6. Conclusions

The participation in the International Project Mont Terri during the last 10 years allowed us to obtain an invaluable background about the knowledge of the pore water chemistry in argillaceous formations. Several water-sampling campaigns were performed in borehole BDI-B1 by means of a quite sophisticated equipment, developed to

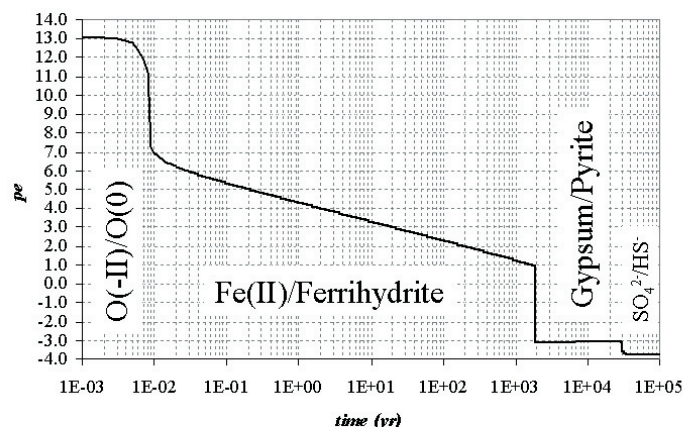


Fig. 17.- pe evolution in the solution for the Oligocene-Miocene Clay. The different pairs controlling the redox are represented.

Fig. 17.- Evolución del pe en la solución. Se representan también la interpretación de los diversos controles ejercidos por los pares redox.

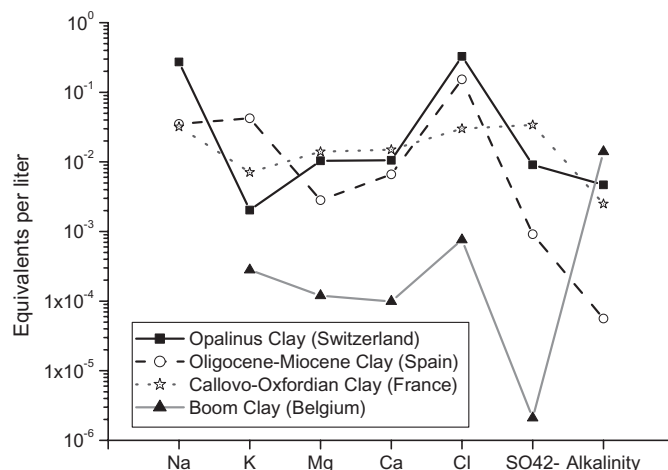


Fig. 18.- Schoeller diagram illustrating the composition of pore waters obtained from mudrocks at different locations.

Fig. 18.- Diagrama de Schoeller que ilustra la composición del agua intersticial de arcillas de diferentes localidades.

Sample	pH	pe	Cl	S	C	Ca	Mg	Na	K	Fe	Si	logP _{CO2(g)}
201	7.64	-3.34	2.4x10 ⁻²	6.7x10 ⁻²	1.3x10 ⁻³	1.1x10 ⁻²	8.3x10 ⁻³	1.2x10 ⁻¹	1.5x10 ⁻³	1.5x10 ⁻⁶	2.7x10 ⁻⁴	-2.87
203	7.52	-3.22	1.8x10 ⁻²	6.2x10 ⁻²	1.7x10 ⁻³	1.1x10 ⁻²	8.4x10 ⁻³	1.1x10 ⁻¹	---	9.9x10 ⁻⁷	2.7x10 ⁻⁴	-2.66
205	7.54	-3.16	2.3x10 ⁻²	7.0x10 ⁻²	1.8x10 ⁻³	1.1x10 ⁻²	8.2x10 ⁻³	1.3x10 ⁻¹	8.2x10 ⁻⁴	1.1x10 ⁻⁵	2.7x10 ⁻⁴	-2.65
253	7.60	-4.02	3.0x10 ⁻²	8.2x10 ⁻²	1.7x10 ⁻³	1.0x10 ⁻²	7.8x10 ⁻³	1.5x10 ⁻¹	8.3x10 ⁻⁴	1.5x10 ⁻⁷	2.7x10 ⁻⁴	-2.72
257	7.12	-3.55	2.3x10 ⁻²	6.9x10 ⁻²	4.6x10 ⁻³	1.1x10 ⁻²	8.5x10 ⁻³	1.5x10 ⁻¹	4.6x10 ⁻⁴	3.0x10 ⁻⁶	2.7x10 ⁻⁴	-1.85
283	6.76	-3.04	5.5x10 ⁻²	8.3x10 ⁻²	8.0x10 ⁻³	1.8x10 ⁻²	1.4x10 ⁻²	1.7x10 ⁻¹	8.1x10 ⁻⁴	4.2x10 ⁻⁶	2.6x10 ⁻⁴	-1.31
290	7.44	-3.92	4.2x10 ⁻²	8.8x10 ⁻²	1.5x10 ⁻³	1.7x10 ⁻²	1.3x10 ⁻²	1.6x10 ⁻¹	7.9x10 ⁻⁴	1.5x10 ⁻⁶	2.6x10 ⁻⁴	-2.64

Table 8.- Modelling output with the reconstructed pore water chemistry (mol/L), including pH, pe and $p\text{CO}_2$ data, for pore waters from Oligocene-Miocene Clay.

Tabla 8.- Resultados de la composición química (mol/L) del agua intersticial para la arcilla del Oligoceno-Mioceno, reconstruida mediante modelización. Se incluyen datos de pH, pe y $p\text{CO}_2$ calculados.

obtain reliable samples and measurements of the pore water from the Opalinus Clay at Mont Terri Rock Laboratory. Avoiding the contact of samples with air showed to be necessary, since this argillaceous rock is extremely susceptible to pyrite oxidation. The successive sampling campaigns and analyses demonstrate the evolution of the physicochemical parameters of the pore water towards a stabilization of the system. Some of the main parameters measured in situ, such as pH, Fe(II), alkalinity and $p\text{CO}_2$, were comparable with previous results obtained by modelling other points of the Opalinus Clay. The modelling results show a reasonable agreement with the measured chemical data. This is true for all constituents except for carbonate concentration and pH, a possible explanation for this disagreement could be related to a CO_2 shift of pore water samples during sampling.

The characterization of the pore waters of clays collected from a borehole of 650 m made in the Oligocene-Miocene Clay, and the vertical distribution of dissolved con-

stituents was made in order to identify sources of waters and water-rock interaction processes. The study of the samples included mineralogical analyses of the rock, cation exchange capacity and exchanger population, chemical analyses of porewater samples and integration of results and modelling using the PHREEQC geochemical code. The evaluation of the fluid composition indicated that oxidation and degassing processes during handling and storage of the samples could have occurred. Taking this into account, the original porewater of the formation was reconstructed by means of modelling, which served as a powerful tool to reconstruct the original water of the formation, taking into account these water-rock interaction processes derived from observations and analyses. Further, a conceptual model on the redox evolution in the Oligocene-Miocene Clay is described as a partial equilibrium process, where the kinetics of sulphate reduction led redox evolution from one equilibrium redox pair to another.

The combination of a precise analytical work together with the geochemical modelling has proven to be useful to characterise these low porosity media and to establish the main sources of uncertainty both in pore water samples obtained in situ from boreholes and from squeezing borehole cores.

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